Tree Growth Rings as Early Indicators of Volcanic Activity on Mt. Etna (Italy)

Dissertation

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von

Ruedi Seiler

aus Trogen, AR

Promotionskommission

Prof. Dr. Markus Egli (Vorsitz)

Dr. Paolo Cherubini (Hauptbetreuer)

Prof. Dr. Max Maisch

Prof. Dr. James Kirchner

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Summary

Volcanoes impose threats on the lives of millions of people, agriculture and infrastructure. Early indicators of volcanic eruptions could improve risk management. However, eruptions remain largely unpredictable. New indicators enabling the prediction of volcanic eruptions well in advance would be useful and are of urgent need. Moreover, the reconstruction of past volcanic activity at many volcanoes would be of great help to landscape management.

Recently, tree stands growing on Mt. Etna (Italy) and on Mt. Nyiragongo (Congo) displayed enhanced photosynthesis along a line prior to volcanic flank eruptions (Houlié et al. 2006). Three to four years later these lines developed into volcanic fissures. The influence of impending eruptions on photosynthesis are currently unknown. However, one explanation could be related to movement of magma in deep conduits of the volcanic system leading to degassing of substances promoting tree growth. Consequently, such tree photosynthetic rates and tree rings, if deemed to be good indicators of tree photosynthetic rates, may be used as early indicators of impending eruptions, and could enable to reconstruct past volcanic eruptions and pre-eruption activity.

The main aims of this thesis were to use tree-ring analyses to assess:

- if the enhanced photosynthetic activity of the trees growing along the volcanic fissure on Mt. Etna could have been caused by climatic conditions,
- if tree-ring chronologies can be used to better understand and possibly reconstruct past volcanic flank eruptions,
- to what extent stable isotope ratios and radiocarbon in tree rings were influenced by pre-eruption degassing.

Manuscript 1 reports on the influence of climate (i.e., temperature and precipitation) on growth of coniferous black-pine stands (*Pinus nigra* JF Arnold) at intermediate elevations on Mt. Etna using tree-ring chronologies from Calabria as a control.

Four different stands at comparable elevation between 1500 and 1700 m were included in this analysis revealing that both temperature and precipitation are not limiting tree growth at intermediate elevation on Mt. Etna. Therefore, the enhanced photosynthesis observed before flank eruptions was not caused by local changes in temperature or water availability.

Manuscript 2 describes tree growth in relation to an anomaly on satellite images related to changes in vegetation activity a couple of months before the 1974 flank eruption on Mt. Etna. To compare tree-growth rates, black pines (*P. nigra*) in a forest stand in the immediate vicinity of the 1974 lava flow, within the anomaly area, and in a control forest stand at comparable elevation but far away from the lava flow were sampled. In combination with available literature these analyses allowed to draw conclusions on the development of the 1974 flank eruption. Further, it could be shown that tree growth was strongly influenced by the eruption during two consecutive years following the eruption, demonstrating that tree-ring chronologies can be successfully used to date past flank eruptions.

Manuscript 3 reports the analysis chemical properties of tree-ring wood of trees growing in a forest stand along the 2002/2003 volcanic fissure. Carbon and oxygen stable isotope composition and radiocarbon content of tree rings in relation to climate variability and the 2002/2003 flank eruption on Mt. Etna revealed that the heavier isotopes of carbon and especially oxygen were strongly reduced during the eruption. Additionally, a reduction of radiocarbon of tree rings formed during two years before the eruption was found not only to coincide with the enhanced photosynthesis previously detected by Houlié et al. (2006), but also to be induced by volcanic degassing depleted in radiocarbon.

This thesis presents an unprecedented, interdisciplinary approach, combining dendrochronology and volcanology, which provided a novel insight into the influence of volcanic activity on tree growth, tree-ring width and chemical information contained in tree rings. This work allowed to disentangle climatic influences from volcanic influences on tree growth as well as to better understand the nature of volcanic influences on trees.

Future interdisciplinary research will allow to further constrain the influence of pre-eruption volcanic activity on trees not only allowing to reconstruct past flank eruptions, but also to better calibrate early warning systems and remote sensing techniques.

Considering new insights from tree-ring research on volcanoes (such as Mt. Etna) may improve the detection of precursory activity by using remote sensing to observe vegetation anomalies.

Zusammenfassung

Vulkane bedeuten eine grosse Gefährdung für das Leben von Millionen von Menschen, für die Landwirtschaft und für Infrastruktur. Frühe Indikatoren von Vulkanausbrüchen könnten zum einen das Gefahrenmanagement und zum anderen die Frühwarnung verbessern.

Bis heute sind Ausbrüche allerdings zum grössten Teil unvorhersehbar. Neue Indikatoren, welche eine frühe Vorhersage von Eruptionen ermöglichen, sind von zentraler Bedeutung und zwingend erforderlich. Zudem würde eine Rekonstruktion vergangener Eruptionen von grossem Interesse für die Landnutzung.

Erst kürzlich wurde berichtet, dass Baumgemeinschaften am Mt. Ätna (Italien) und auf dem Mt. Nyiragongo (Kongo) vor Flankeneruptionen entlang bestimmter Wachstumslinien eine erhöhte Photosynthese aufwiesen (Houlié et al., 2006). Drei bis vier Jahre später entwickelten sich diese Linien in vulkanische Bruchspalten. Der Einfluss von anstehenden Eruptionen auf die Photosynthese der Bäume ist zur Zeit nicht bekannt. Eine mögliche Erklärung für die erhöhte Photosynthese könnte im Zusammenhang mit Bewegungen von Magma in den unterirdischen Verbindungskanälen des Vulkansystems stehen. Die dadurch geförderten vulkanischen Gase, versetzt mit Substanzen, welche dem Baumwachstum zuträglich sind, gelangen so an die Oberfläche. Demzufolge könnten Photosynthese und Baumwachstum (direkt mit der Photosynthese zusammenhängend) als frühe Indikatoren für anstehende Eruptionen dienen und die Rekonstruktion vergangener Eruptionen ermöglichen.

Die Hauptziele dieser Dissertation waren es, anhand von Jahrringanalysen zu verstehen:

- ob die erhöhte Photosynthese der Bäume entlang der vulkanischen Bruchlinie auf dem Mt. Ätna vom Klima hätte hervorgerufen werden können,
- ob Jahrring-Chronologien verwendet werden können, um vulkanische Flanken-eruptionen besser zu verstehen und möglicherweise zu rekonstruieren,
- in welchem Ausmass stabile Isotopenverhältnisse und Radiokohlenstoff in Jahrringen von aufsteigenden Gasen vor der Eruption beeinflusst wurden.

Manuscript 1 widmet sich dem Einfluss des Klimas (i.e., Temperatur und Niederschlag) auf das Wachstum von Nadelbäumen der Schwarzkiefer (*Pinus nigra* JF Arnold) auf mittleren Höhenlagen am Mt. Ätna. Als Kontrolle werden Jahrring-Chronologien von Kalabrien (Italien) als Kontrolldaten verwendet.

Vier verschiedene Baumpopulationen auf vergleichbarer Höhe zwischen 1500 m und 1700 m wurden in die Untersuchung miteinbezogen welche ergab, dass sowohl Temperatur als auch Niederschlag für das Wachstum der Bäume auf dieser Höhenlage am Ätna nicht limitierend wirken. Daraus kann gefolgert werden, dass die erhöhte Photosynthese, welche vor der Flankeneruption beobachtet wurde weder durch eine Veränderung der Umgebungstemperatur, noch durch eine erhöhte Verfügbarkeit von Feuchtigkeit oder Wasser ausgelöst wurde.

Manuscript 2 beschreibt das Baumwachstum im Zusammenhang mit einer Infrarot-Anomalie, welche durch eine Verringerung der Vegetationsaktivität ein paar Monate vor der 1974 Flankeneruption auf dem Mt. Ätna hervorgerufen wurde. Für die Untersuchung wurden die Wachstumsraten des beeinflussten Baumbestandes (*P. nigra*) mit dem Wachstum von Bäumen der selben Art fernab von der Eruptionsstelle auf vergleichbarer Höhe verglichen. In Kombination mit Veröffentlichungen über den Hergang dieser Eruption konnten die Baumproben dazu verendet werden, die Entwicklung der 1974 Eruption besser zu verstehen. Zudem konnte gezeigt werden, dass das Baumwachstum während zwei Jahren unmittelbar nach der Eruption stark beeinflusst wurde. Die Jahrringe waren signifikant schmaler oder fehlten ganz. Diese Beobachtung zeigt, dass Jahrring-Chronologien sehr wohl Auskunft über den Zeitpunkt von Flankeneruptionen in der Vergangenheit Auskunft geben könten.

Manuscript 3 berichtet von den chemischen Analysen des Holzmaterials einzelner Jahrringe der Bäume, welche entlang der 2002/2003 Eruptionsbruchzone wuchsen. Stabile Isotopenverhältnisse von Kohlenstoff (C) und Sauerstoff (O) im Holzmaterial haben gezeigt, dass die schwereren Isotope von Kohlenstoff und speziell von Sauerstoff während der Eruption stark untervertreten waren. Das Klima konnte auch hier als mögliche Ursache ausgeschlossen werden. Zudem konnte eine Reduktion von Radiokohlenstoff in den Jahrringen während zwei Jahren vor dem Ausbruch beobachtet werden. Diese Zeitspanne stimmt exakt mit der Phase der erhöhten Photosynthese (Houlié et al., 2006) überein und könnte deshalb durch vor der Eruption aufsteigende, vulkanische Gase, welche kein Radiokohlenstoff enthalten, verursacht worden sein.

Diese Dissertation verkörpert einen neuartigen, interdisziplinären Ansatz, welcher die Dendrochronologie mit der Vulkanologie zusammen bringt, um neue Einsichten in den Einfluss vulkanischer Aktivität auf das Baumwachstum, die Jahrringbreiten und die chemische Eigenschaften in den Jahrringen zu erlangen. Diese Arbeit ermöglicht es, die klimatischen Einflüsse von den vulkanischen Einflüssen zu trennen und die Beschaffenheit des vulkanischen Einflusses auf die Bäume am Mt. Ätna besser zu verstehen.

Zukünftige interdisziplinäre Forschung wird es ermöglichen, vergangene Flankeneruptionen zu rekonstruieren und zudem die Frühwarnsysteme, basierend auf Satellitenbildmessungen, zu verbessern.

Satellitengestütze Vegetationsbeobachtung könnte unter Berücksichtigung neugewonnener Erkenntnisse aus der Baumringforschung auf Vulkanen (wie z.B. Mt. Ätna) darauf optimiert werden Vorzeichen vulkanischer Aktivität zu erkennen.

Content

Abbreviations and definitions

NDVI = Normalized Difference in Vegetation Index. The index is calculated using the red and near-infrared band to depict vegetation greenness

NIR = Near Infra Red. The near infrared reflection highlights heat and vegetation greenness

tree rings = annual tree-growth increments

flank eruption = volcanic eruption occurring on the flanks of the volcano

volcanic fissure = eruptive surface fracture caused by volcanic activity

pre-eruption activity = volcanic activity occurring before the surface eruption

$\delta^{18}O$ = ratio of the heavy (^{18}O) and the lighter (^{16}O) oxygen isotope

$\delta^{13}C$ = ratio of the heavy (^{13}C) and the lighter (^{12}C) carbon isotope

^{14}C (radiocarbon) = radioactive (^{14}C) carbon isotope

About this work: including authors' contributions

This is a cumulative thesis, based on three individual manuscripts:

1. Seiler R, Kirchner JW, Krusic PJ, Tognetti R, Houlié N, Andronico D, Cullotta S, Egli M, D'Arrigo R, Cherubini P. 2017. Insensitivity of tree-ring growth to temperature and precipitation sharpens the puzzle of enhanced pre-eruption NDVI on Mt. Etna (Italy). PLoS ONE 12(1):e0169297. doi:10.1371/journal.pone.0169297

Contributions of the PhD candidate: Conceptualization, data collection, data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing of the original draft, reviewing and editing.

2. Seiler R, Houlié N, Cherubini P. 2017. Tree growth reveals the development of the 1974 Mt. Etna eruption. Scientific Reports 7:44019. doi:10.1038/srep44019

Contributions of the PhD candidate: Conceptualization, data collection, data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing of the original draft, reviewing and editing.

3. Seiler R, Hajdas I, Saurer M, Kirchner JW, Houlié N, Cherubini P. 2017. Tree-ring stable isotopes and radiocarbon reveal pre- and post effects of volcanic eruptions on trees at Mt. Etna (Italy). Chemical Geology (in preparation)

Contributions of the PhD candidate: Conceptualization, data collection, data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing of the original draft, reviewing and editing.

Part A introduces the scientific background for this project, presents the main findings and provides an outlook for future research. Part B comprises the acknowledgements and the authors curriculum vitae (CV). Detailed results, interpretation and discussion can be found in the full manuscripts in part C.

Paolo Cherubini (WSL), Markus Egli (UZH), Irka Hajdas (ETHZ), Matthias Saurer (PSI), Nicolas Houlié (ETHZ) and James Kirchner (ETHZ) not only proposed this research project, but further greatly supported conceptual work, fieldwork, laboratory work, data analysis and interpretation as well as manuscript writing.

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Francesca Moergeli did part of the laboratory sample preparation for the isotope analyses. Vincenzo Crimi and his colleagues from Corpo Forestale (Bronte) provided access and permission to carry out the fieldwork on Mt. Etna.

Ruedi Seiler prepared three fieldwork campaigns, conducted the fieldwork and the laboratory work, carried out the analyses and the interpretation of the results and crafted the manuscripts.

All authors contributed and greatly contributed to the final manuscript versions.

Part A: Synopsis

Introduction

1 Volcanic eruptions and monitoring

A large number of phenomena related to volcanic activity reaching from explosive eruptions, lava flows, wildfires, degassing to ash deposition are affecting settlements, forests, orchards and infrastructure or are influencing airplane traffic (Ewert et al., 2005).
The livelihood of more than four million people worldwide is affected by volcanic activity and the average economic damage caused by volcanic eruptions exceeds 98 million US dollars each year (Statistic Brain Research Institute Online, 2017). Increasing accumulation of infrastructure and population in affected areas call for a better understanding of the evolution of volcanic eruptions (Ewert et al., 2005; Grotzinger et al., 2008).
Anticipation of volcanic eruptions require monitoring of active volcanoes by measuring various physical and chemical parameters which capture volcanic unrest related to subsurface magma movement (Ewert et al., 2005).
Volcanic activity most often occurs along the borders of tectonic plates, predominantly along subducting, spreading or convergent zones where tectonic plates are moving towards, against or lateral to each other (Goudie, 2007). The great majority of magmas are produced at spreading ridges, subduction zones or so-called "hot spots" (Scaillet et al., 2003). Predominant types of volcanoes, such as stratovolcanoes, shieldvolcanoes, domevolcanoes or composite volcanoes, can be distinguished based on their morphology, the magma source and in the way they develop (Grotzinger et al., 2008; Goudie, 2007).
Mt. Etna is the highest stratovolcano in central and western Europe with an elevation of about 3300 m (Chester et al., 1985; Kieffer & Tanguy, 1993; Tanguy et al., 1997). It is located close to a subduction zone on top of the border between two converging plates, the African plate and the Eurasian plate (Caputo et al., 1970; Gasparini et al., 1982; Ellam et al., 1989; Tanguy et al., 1997), separating the Hyblean Plateau crust carrying Sicily (Burollet et al., 1978) from the oceanic crust of the Ionian basin (Figure 1; Makris et al., 1986). Because of the rather complicated tectonic setting below Sicily, the origin and the propagation of Mt. Etna is not fully understood and there are different theories on the development of the volcano (Monaco et al., 2005). Rittmann (1973) proposed that Mt.

Etna originated from the intersection of three main fault zones, McGuire & Pullen (1989), McGuire et al. (1990) and Bousquet & Lanzafame (2001) related the orogenesis (i.e. formation of the mountain) to a gravitational spreading. In contrast, others presume it developed as a "hot spot" (Tanguy et al., 1997; Clocchiatti et al., 1998), a volcano unrelated to a tectonic plate boundary (OSU online, 2017). Further may trending of the fault zones (Frazzetta & Villari, 1981; Lo Giudice & Rasa, 1986; Lanzafame & Bousquet, 1997) or extentional processes (Trapponnier, 1977; Ellis & King, 1991; Monaco et al., 1997) have been responsible for the orogenesis (Grotzinger et al., 2008).
Below Sicily, the extensive subduction process along the tectonic border between the African and the Eurasian plate results in a E-W distention (Figure 1), therefore, there is no subduction (Tanguy et al., 1997), but rather extentional tectonics which dominate volcanic activity on Mt. Etna (Monaco et al., 2005). This circumstance is supported by seismic investigations (Anderson & Jackson, 1987; Selvaggi & Chiarabba, 1995).

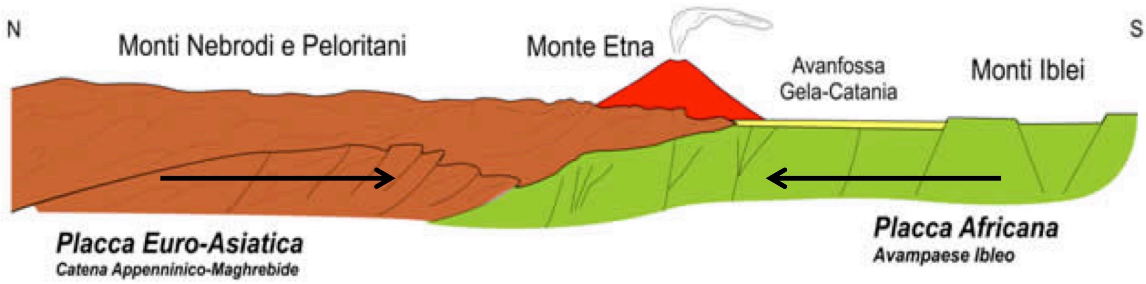

Figure 1 *Border of the Eurasean and African Plate on which Mt. Etna is located (VUME Online, 2017)*

After the pre-Etnean Gulf disappeared, the Mt. Etna edifice developed in a series of overlapping stratovolcanoes created over five known stages (Figure 2; Rittmann, 1973; Condomines et al., 1995) by the accumulation of basaltic lava flows and pyroclasts (Monaco et al., 1997) during the past 300'000 years.

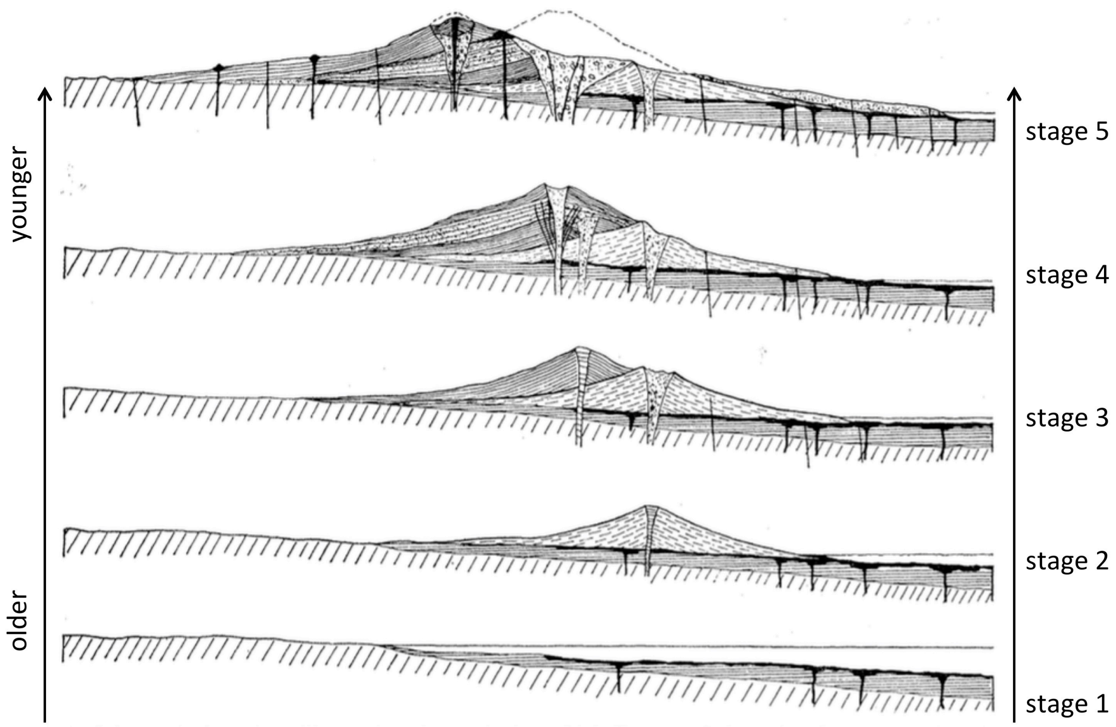

Figure 2 Orogenesis of Mt. Etna over the five known stages (stage 1 to 5) according to Rittman's classification (Rittmann, 1973)

Today, volcanic activity on Mt. Etna predominantly occurs along the base of the eastern flank. Several faults leading towards the NNW and the NNE (e.g., the Pernicana fault; Figure 3) are associated with shallow depth seismicity and earthquakes sometimes leading to surface eruptions along eruptive fissures (Monaco et al., 1997). Most fissures develop along the northeastern and south-southeastern flanks (Monaco et al., 1997).

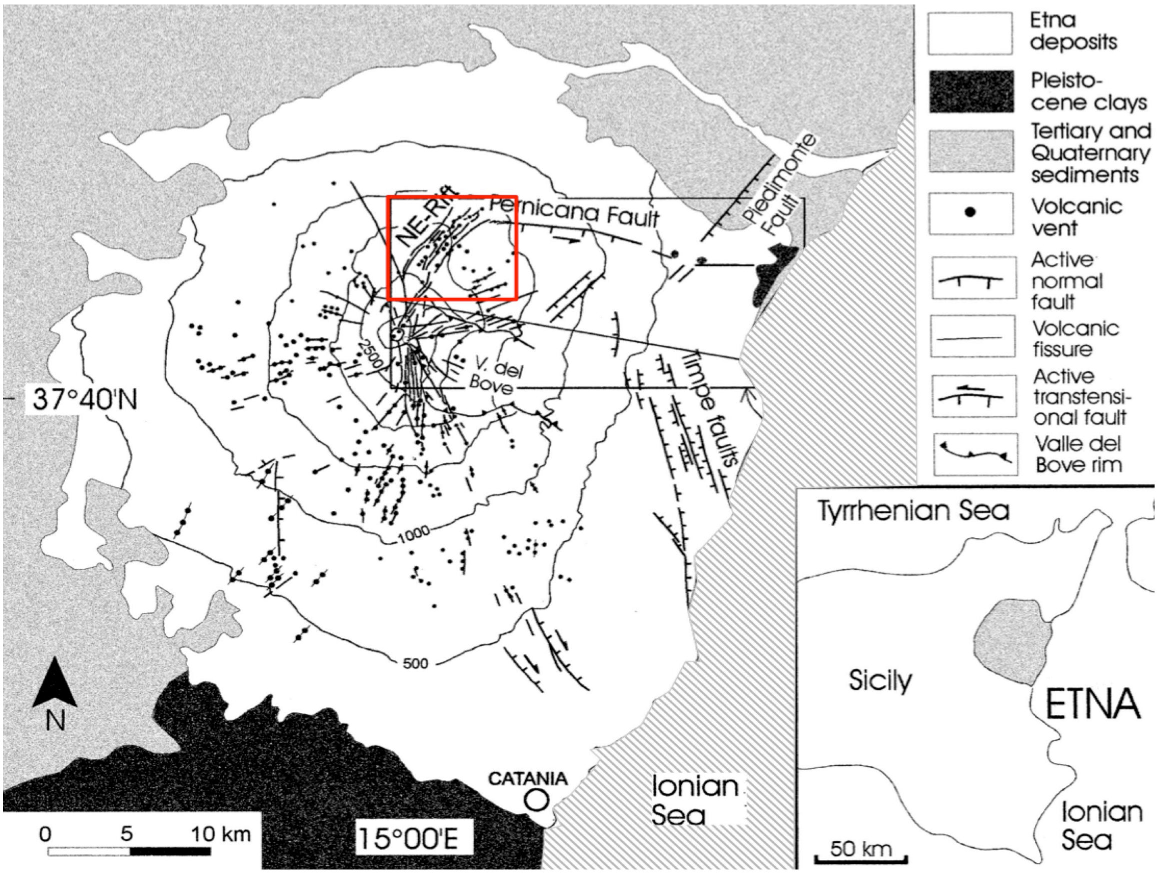

Figure 3 *Volcanic surface fault structures, the NE-rift and the Pernicana fault on Mt. Etna (Tibaldi & Groppelli, 2002). The area depicted in Figure 4 is indicated in red.*

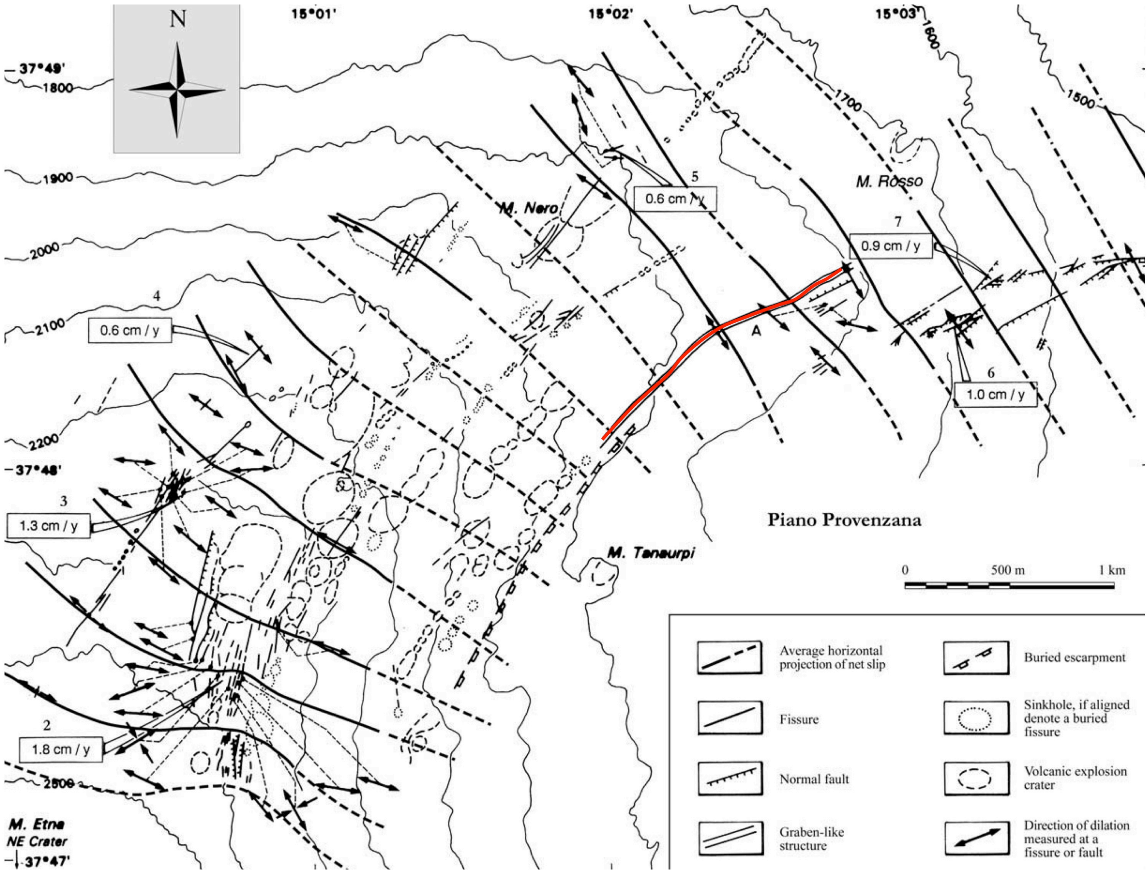

Figure 4 Detailed rift zones in the area marked in Figure 3 of Piano Provenzana *(Tibaldi & Groppelli, 2002). The red line indicates the 2002/2003 fissure.*

Along these fissures, the type of eruption is determined by the amount of volatiles (gasses and H_2O) the erupting magma batch contains. While higher gas and water contents in the magma lead to more explosive eruptions due to expansion of enclosed gasses under decreasing pressure, low contents of gas result in effusive eruption types (Scaillet et al., 2003). Gasses and water which are exsolved from the magma due to reducing pressure during the rise inside the volcano often times rise ahead of the magma and are degassed at the surface before the eruption occurs (Scaillet et al., 2003; Aubert, 1999).

On Mt. Etna (Sicily) effusive eruptions during which magma is emitted at the main crater and/or on the flanks are observed most often. Resulting lava flows originating from the Pernicana fault at Piano Provenzana for instance (Figure 4) sometimes proceed to low-elevation, densely-populated and agriculturally managed areas, endangering infrastructure and livelihood (Tilling, 1991; Tibaldi & Groppelli, 2002; Tilling, 2008; Tilling 2009).

Improving predictions of volcanic eruptions, such as flank eruptions, which may lead to subsequent lava flows reaching agricultural areas, settlements and villages (Tibaldi & Groppelli, 2002) is of great importance for the assessment of natural hazards and for early warning.

Apart from predicting impending eruptions, volcanic monitoring provides useful tools to comprehend the eruptive processes taking place inside a volcanic plumbing system (Tilling, 2008). Volcanic monitoring typically consists of the acquisition of different parameters, mainly geological, geochemical and geophysical phenomena, as well as seismic, geodetic, gravitational, magnetic, geoelectrical, or surface degassing and temperature anomalies, acquired by different measurement techniques as well as the analysis of their variations over time (e.g., Andronico et al., 2009 and reference therein; McNutt et al., 2000, Tilling, 2008). The analysis of different monitored parameters further provides a multidisciplinary insight into both the unrest of dormant volcanoes and the evolution of ongoing eruptions (e.g., Andronico et al., 2005), reinforcing the assessment of the volcanic hazards.

The best precursors for basaltic volcanoes, like Mt. Etna on Sicily, typically characterized by high-frequency eruptions, mainly include seismic signals both earthquakes and primarily volcanic tremor (Grotzinger et al., 2008; Alparone et al., 2003) and gas-emission measurements (Aiuppa et al., 2007),

Even though scientists are using abovementioned techniques to often successfully predict eruptions, in many cases the resulting prognoses reveal the following shortcomings:

a) predictions can only be made **shortly in advance** and

b) eruptions often occur at **unknown locations**, making it difficult to adequately restrict hazardous zones, warn the population and take precautionary measures in affected areas.

c) Therefore, the **reconstruction of past events** is needed to further improve the understanding about the development of eruptions.

In addition to previously mentioned parameters, longer term predictors to volcanic eruptions and predictive tools enabling to indicate risk perimeters could, therefore, greatly improve risk assessment and early warning systems (McNutt et al., 2000).

Only recently, a locally confined, enhanced Normalized Difference in Vegetation Index (NDVI), considered to closely represent vegetation photosynthesis (Dobbertin, 2005), was measured during two consecutive years before the 2002/2003 flank eruption on Mt. Etna (Houlié et al., 2006), suggesting that tree growth was affected by volcanic activity before the eruption. Interestingly, the enhanced NDVI signal was measured along a regionally confined line. During the consequent eruption starting in October 2002, this line developed into an eruptive fissure (Figure 5). A comparable detection of increased NDVI prior to eruption was made in Kongo on Mt. Niyragongo in 2002 (Houlié et al., 2006), supporting the evidence of enhanced tree growth before eruptions.

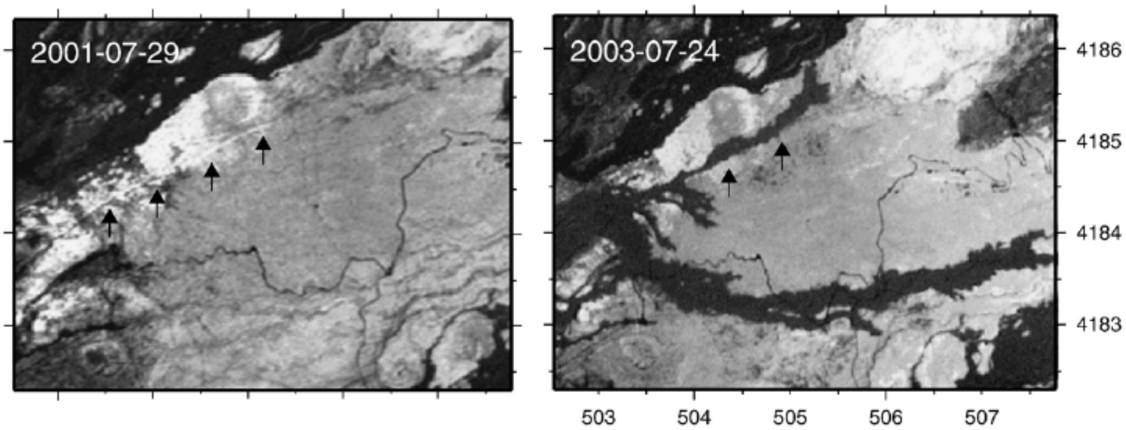

Figure 5 *Aerial image showing the bright NDVI anomaly line (left) and the black lava flow after the 2002/2003 fissure eruption along the same line (right). The exact location is marked in Figure 4.*

Opposed to these observations, a reduced near infrared reflectance (NIR), detected before the onset of the 1974 flank eruption on Mt. Etna was reported and interpreted as a negative influence of volcanic activity on trees before the surface eruption (De Carolis et al., 1975). Such negative influences were also reported at Mammoth Mountain in California where extensive degassing of CO_2 lead to tree die-off (Farrar et al., 1995) and at Pino del Nambroque volcano on La Palma (Spain), where trees were killed at a confined location one year before an eruption (Figure 6; Romero & Bonelli, 1951).
These findings strongly suggest that trees are influenced by volcanic activity sometimes well before surface eruptions occur.

Mt. Nyiragongo (Congo)

Mammoth lake, California (USA)

Pico del Nambroque, La Palma (Spain)

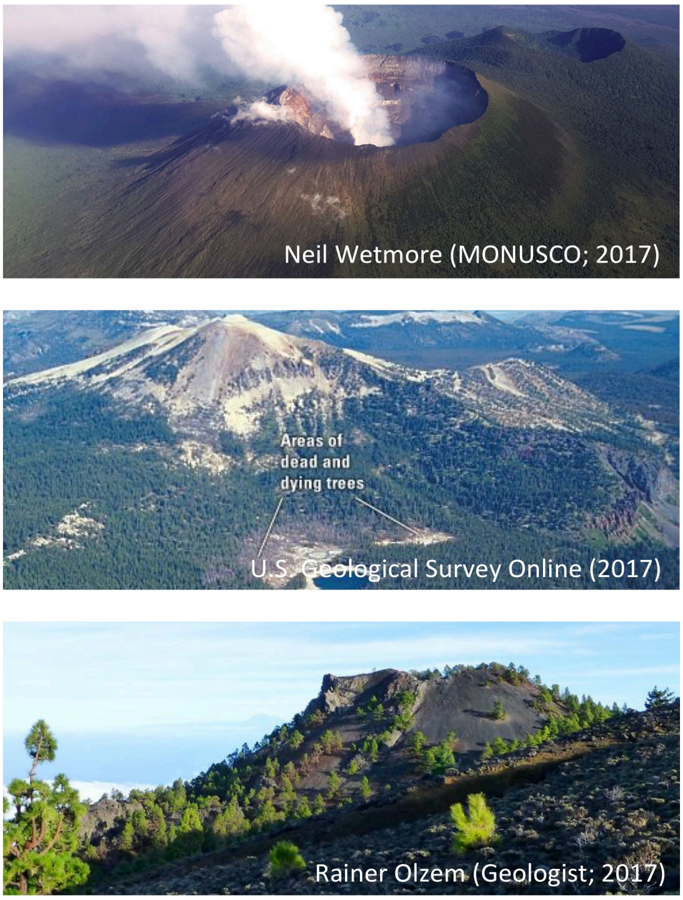

Figure 6 Further volcanoes on which vegetation anomalies related to volcanic activity were observed.

At Mt. Nyiragongo (Congo) no further studies analyzing the origin of the vegetation anomaly detected by remote sensing (Houlié et al., 2006) were conducted. At Mammoth lake (California, USA) studies showed that trees died due to overexposure to volcanic CO_2 degassing (Cook et al., 2001). As for Pico del Nambroque (La Palma, Spain), the phenomenon of tree die-off is described and reported (Romero & Bonelli, 1951), however, there were no further investigations on the cause of the event.

Therefore, tree-ring analyses could disclose valuable insights towards understanding the influence of pre-eruption volcanic activity and its effect on tree growth.

2 Dendrochronology

Dendrochronology, from the ancient Greek dendron (δένδρον; wood), chronos (χρόνος; time) and logos (λόγος; word, reason or plan) is the study of annually formed tree rings and information contained therein over time. Under temperate climate conditions, characterized by regular seasonality most trees grow in annual cycles building growth rings during the vegetation season by producing starch/sugar via photosynthesis, forming woody cells from spring to autumn, before stopping growth again during winter (Schweingruber, 1996). Such tree-growth rings can be divided into different types of cells; earlywood cells, built during the spring and early summer season are characterized by large vessels and thin cell-walls allowing nutrient and water transport (Schweingruber, 1996; Uggla et al., 2001), whereas latewood cells are built towards the end of the vegetation season by forming thicker cell-walls and smaller vessels for tree-stabilizing purposes (Schweingruber, 1996; Uggla et al., 2001). Elements and molecules allocated to an annual increment during any given vegetation season are fixed within the wood structure (McCarroll & Loader, 2004). Therefore, tree rings provide an annually resolved natural archive storing information on past environmental conditions.

Tree-ring analyses have been widely applied in a diverse array of scientific research fields, related to climatic, ecological or archaeological research questions (e.g., Levin & Kromer, 2004; Francey & Farquhar, 1982; Duquesnay et al., 1998; Porter et al., 2009).

Most prominent applications are studies on tree-ring width and wood density, which allow to assess past temperature and precipitation variability, past climate conditions or tree-stand dynamics and many more. Further, wood-anatomical features (e.g., cellwall thickness) or bioecophysiological information (e.g., nutrients, stable and radioactive isotopes, particles) contained within the woody structure of tree rings can be analyzed to address research topics, such as climate sensitivity, water origin or water use efficiency of trees during the past. Furthermore, tree-ring analyses are frequently used for dating purposes of archeological or historical wood findings (Baillie, 2015).

Providing such a great variety of annually resolved environmental information tree rings have been frequently used to assess influences of volcanic eruptions on trees. Bigger eruptions (e.g., Mt. Pinatubo in 1991) expel a large amount of fumaroles, often leading to an increase of cloud coverage, hence limiting sun exposition and photosynthesis, resulting in small growth rings, which have been found in trees worldwide (e.g., Scuderi, 1990; Breitenmoser et al., 2012). Smaller eruptions often affect tree growth at a regionally confined scale. For example were isotopic ratios in tree rings found to be influenced by an eruption of Stromboli in Italy (Battipaglia et al., 2007).

However, tree-ring width has never been used to assess the influence of pre-eruption volcanic activity on trees.

3 Methods

Tree-ring analysis

To evaluate growth patterns of trees sampled along the eruptive fissures on Mt. Etna I applied standard dendrochronology to measure annual tree-growth increments using a binocular microscope coupled to a measuring table and a computer running a time series analysis software. The obtained tree-ring width measurements (i.e. tree-growth time series) were then visually and statistically crossdated (Holmes, 1983). This crossdating (i.e., statistical comparison of single tree-ring width series with a mean chronology) is applied to detect shifts or missing rings in any single tree-ring width series and provides annually dated tree-growth measurements. Only after proper crossdating can tree-ring chronologies be used for further analyses (Fritts, 1976).

Climate modeling

Standard dendroclimatology analyzes the influence of a single parameter related to climate variability (e.g., temperature, precipitation, drought, cloud-coverage and further more) on tree growth. Thereby, the direct correlation of each climate parameter with the tree-ring chronology represents the influence that parameter has on the growth of the trees in a certain area. Opposed to that, climate modeling combines different climate parameters to so called "mixed effect models" trying to model tree-ring width variability. At intermediate elevations tree growth is usually influenced by more than just one single limiting parameter. Therefore, climate models incorporating multiple parameters are able to jointly explain a larger portion of tree-growth variability than what could be derived from standard dendroclimatological analysis (Cook & Kariukstis, 1990; Seiler et al., 2017).

This thesis presents results from simple correlations and climate modeling, which are discussed in Manuscript I.

Tree-ring chemistry

Wood material, from tree cores which have been measured and properly crossdated, can be analyzed for their chemical composition. Such dendrochemistry allows to reconstruct growth condition (e.g., atmospheric or soil composition) during the year in which the analyzed tree ring was growing. By extracting the chemical composition of several, consecutive growth rings it is possible to quantify the influence of known eruptions on trees, or to detect and date unknown eruptions from the past by the chemical traces they caused in particular tree rings (Levin & Kromer, 2004).

4 Motivation and Structure of the Thesis

Previously introduced findings of remote sensing suggest that vegetation can be affected by volcanic activity even before surface eruptions occur. Therefore, trees growing along fissures of past flank eruptions along the flanks of Mt. Etna are particularly suitable to be analyzed in combination with the reported NDVI related to the 2002/2003 flank eruption (Figure 7) and the measured NIR signal preceding the 1974 flank eruption.

Figure 7 The 2002/2003 fissure at Piano Provenzana showing an affected P. nigra tree stand within the lava flow (Photograph: R. Seiler, 2013).

On Mt. Etna flank eruptions predominantly occur within an elevation belt of approximately 1600 to 2500 m above sea level (e.g., Tibaldi & Groppelli, 2002), where *Pinus nigra* JF Arnold is the predominant tree species.

P. nigra growing in the Mediterranean region is most abundant between 800 and 1200 m with its upper border lying at roughly 1800 to 2000 m (Schweingruber, 1993). It is an evergreen conifer reaching heights of up to 30m (Banfi & Consolino 2009; Kremer, 2010). Developing wide rings with clear borders between the latewood of one year to the earlywood of the subsequent year and with a life-span of more than 400 years (Roloff et al., 2008), *P. nigra* is particularly suitable for dendrochronological studies (Schweingruber, 2003).

For this research study we used samples of *P. nigra* growing at intermediate elevations at ~1800 m on Mt. Etna and along the eruptive fissures of 2002/2003 and 1974 (Figure 8).

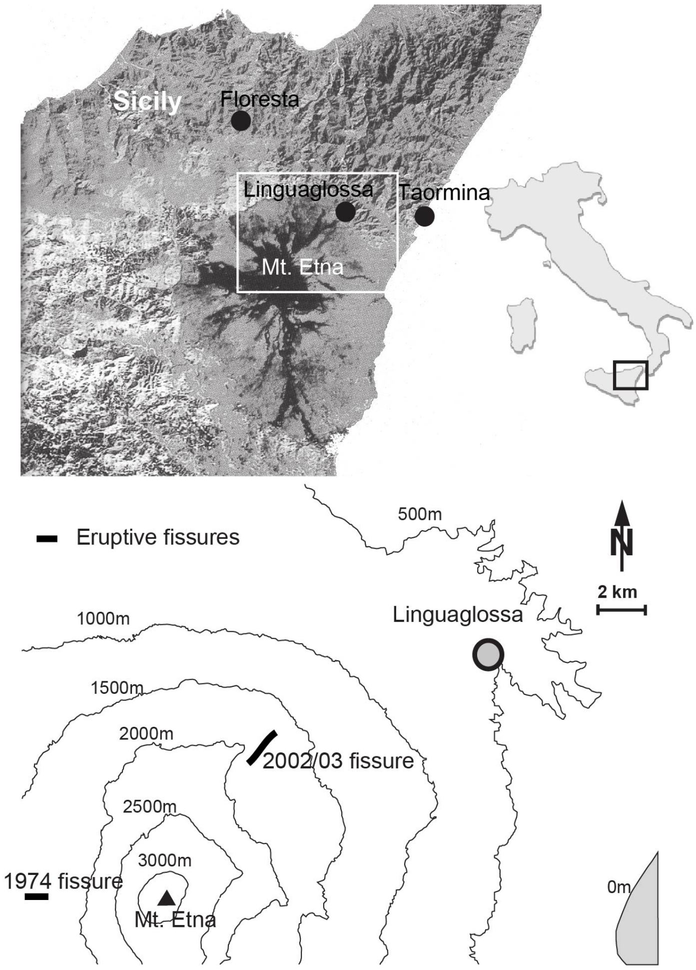

Figure 8 *Investigation area on Mt. Etna (Sicily) displaying the two eruptive fissures of 1974 on the western flank and 2002/2003 on the north-eastern flank (basis map from Egli et al., 2007).*

In contrast to previous studies analyzing large-scale, post-eruption effects on trees, such as effects of large eruptions on trees worldwide, tree rings and information therein have never been studied for their signal of pre-eruption volcanic activity.

Therefore, our aims were to analyze tree-ring width and information stored in tree rings (Figure 9) in relation to pre-eruption volcanic activity on Mt. Etna.

Figure 9 *Cores from trees (P. nigra) growing along the 2002/2003 Mt. Etna fissure (Photograph R. Seiler, 2014).*

By analyzing trees growing along the eruptive fissures of 2002/2003 and 1974 we addressed the following research questions (RQ):

RQ 1) Could the availability of additional water or an increase in surrounding temperatures induced by volcanic activity preceding the 2002/2003 flank eruption on Mt. Etna have caused the observed increase in NDVI? ➔ Manuscript 1

RQ 2) How can tree rings be used to better understand the development of the 1974 flank eruption on Mt. Etna? ➔ Manuscript 2

RQ 3) Are carbon and oxygen stable isotopes and radiocarbon in tree rings influenced by volcanic activity before and during the 2002/2003 eruption? ➔ Manuscript 3

The subsequent chapters are composed of separately published papers in ISI journals each focusing on one of the research questions laid out above and contributing to the stated research aim.

Manuscript 1 *"Insensitivity of tree-ring growth to temperature and precipitation sharpens the puzzle of enhanced pre-eruption NDVI on Mt. Etna (Italy)"*

Tree growth at high elevations is usually limited by temperature (Büntgen et al., 2006; Briffa et al., 2013), whereas in the Mediterranean it is known to be primarily limited by precipitation (i.e., water availability) and is, therefore, enhanced during wet years (Cherubini et al., 2003, Gea-Izquierdo et al. 2011). Further, does the enhanced NDVI signal recorded preceding the 2002/2003 flank eruption at Piano Provenzana (Houlié et al., 2006) suggest, that trees may have benefited from changes of local temperature and water conditions preceding the eruption on Mt. Etna.

We therefore hypothesize that:

i)	Tree growth at intermediate elevation on Mt. Etna is sensitive to temperature and precipitation.

ii)	Consequently, increased local ambient temperatures or additional water provided by pre-eruption volcanic activity (e.g., volcanic degassing) may have supported tree growth causing the NDVI anomaly along the locally confined fissure line.

To assess the hypotheses we sampled (n≈500) tree cores from four different locations at intermediate elevations on Mt. Etna to quantify climate sensitivity of trees (i.e., sensitivity to precipitation, temperature and drought) in order to assess if local changes of temperature or water availability could have caused the NDVI signal.

Manuscript 2 *"Tree-ring width reveals the development of the 1974 Mt. Etna eruption"*

Several studies report that vegetation can be affected by pre-eruption volcanic activity both positively (Houlié et al., 2006) and negatively (DeCarolis et al., 1975; Sorey et al., 1998; Romero & Bonelli, 1951). Therefore, local changes in NDVI (Houlié et al., 2006) or NIR (DeCarolis et al., 1975) which were reported before flank eruptions are most likely related to tree growth.

Therefore, we hypothesize:

iii) If the factors which caused the NIR anomaly, observed during September 1973, were acting over an extended time period, they must have influenced the growth of the trees growing in the area. This effect would, as a consequence, be visible in tree rings.

iv) Therefore, tree rings may provide better understanding of eruption developments.

v) Further, tree-ring chronologies can be used to date past volcanic flank eruptions.

To assess the hypotheses we analyzed tree cores of trees growing along the 1974 - Monte de Fiore fissure, within the area constrained by the NIR anomaly to calculate tree-growth rates before and during the eruption years and to combine our findings with volcanological observations reported in literature.

Manuscript 3 *"Tree-ring stable isotopes and radiocarbon reveal pre- and post effects of volcanic eruptions on trees at Mt. Etna (Italy)"*

Ratios of the carbon (^{13}C) and oxygen (^{18}O) stable isotopes in tree rings reflect a combination of atmospheric composition and tree-physiological responses to environmental changes allowing to assess the influence of climate conditions over time (Francey & Farquhar, 1982; Duquesnay et al., 1998; Porter et al., 2009) or to draw conclusions on the water source trees were using (Ehleringer & Dawson, 1992; Lee et al., 2007; Leonelli et al., 2017). Given the pre-eruption influence of volcanic activity on vegetation we hypothesize that:

vi) Trees have captured changes in stable isotopic ratios of carbon and oxygen induced by pre-eruption volcanic activity preceding the 1974 Monte de Fiore eruption.

vii) Trees have taken up increased levels of CO_2 from volcanic gasses before the eruption leading to reduced values of ^{14}C in tree rings.

To asses the hypotheses we analyzed stable isotopic ratios and ^{14}C content in cellulose from wood material of separate tree rings. Further, we made climate analyses to account for changes in stable isotope ratios induced by climate variability.

Discussion and Conclusion

In this thesis results of a dendrochronological study on trees growing along two eruptive fissures (1974 and 2002/2003) on Mt. Etna are presented.

This project includes tree-ring analyses to study pre-eruption activity, a joint assessment of conventional precursor monitoring data (i.e., seismicity and crystallography) as well as the analyses of stable isotopic ratios and radiocarbon content of single tree rings and, therefore, largely improves the understanding of how trees were affected (e.g., changes in tree-ring width or isotopic- and radiocarbon signature in tree-ring material) during the development of past volcanic eruptions.

We performed dendroclimatological analyses and climate modeling to assess the influence of precipitation and temperature on tree growth. Further, we jointly interpreted pre-eruption remote-sensing, seismic and crystallographic observations together with tree-ring width analysis, demonstrating that tree rings can be used to better understand pre-eruption activity of single flank eruption events. Finally, we found evidence that trees may have taken up volcanic CO_2, stimulating tree growth and causing the enhanced NDVI signal observed before the 2002/2003 flank eruption.

Basing on our results, airborne remote-sensing monitoring of trees growing on volcanoes may be applied and included in early warning systems allowing to

a) **anticipate volcanic eruptions** farther ahead of time,
b) constrain the **location of eruptions**, and
c) **reconstruct past eruptions** of volcanoes for which the history is not known.

In the following, the outcome of this research project is divided into three respective manuscripts answering the outlined research questions (RQ) as well as the hypotheses.

Chapter 1 *"Insensitivity of tree-ring growth to temperature and precipitation sharpens the puzzle of enhanced pre-eruption NDVI on Mt. Etna (Italy)"*

RQ 1) Could the availability of additional water or an increase in surrounding temperatures induced by volcanic activity preceding the 2002/2003 flank eruption on Mt. Etna have caused the observed increase in NDVI? ➔ Manuscript 1

Based on our findings this first research question has to be answered with **NO.**

Results of our analyses showed that tree growth at intermediate to high elevations on Mt. Etna is not strongly limited by precipitation and temperature. The climatic influence is even slightly weaker compared to a control region of similar weather conditions and elevation in Calabria (Southern Italy). Further, did the application of climate models reveal that the weak influence of precipitation and temperature on tree growth on Mt. Etna is not consistent over time.

Therefore, we concluded that tree growth at intermediate to high elevations on Mt. Etna is not limited by climate, nor is the climate influence very strong. Thus, the upper treeline on Mt. Etna is not determined by climate conditions as in the European alps for example (e.g., Büntgen et al., 2006), but it is rather limited by volcanic activity such as frequent lava flows and consequent wildfires.

On one hand, Mt. Etna's treeline is too low for tree rings to be limited by summer temperature. On the other hand, the treeline is too high for summer drought to be the limiting factor as is the case in the Mediterranean lowlands (e.g., Cherubini et al., 2003; Maselli et al., 2014).

Tree-growth variability at intermediate elevation on Mt. Etna, which lies between the high elevation where temperature would be limiting and the low elevation where summer drought is limiting cannot be explained using meteorological data.

Therefore we have to reject our first hypothesis:

i) Tree growth at intermediate elevation on Mt. Etna is sensitive to temperature and precipitation.

➔ to be REJECTED

Based on the insensitivity of tree growth to precipitation and temperature among trees growing along the 2002/2003 eruptive fissure in Piano Provenzana we conclude that an increase in local ambient air or soil temperatures induced by pre-eruption volcanic activity would not have stimulated tree growth before the eruption and is, therefore, not the cause of the NDVI anomaly.

Further, would an additional water/moisture availability provided by pre-eruption volcanic activity not have caused an increase in tree growth.

Therefore, we can also reject our second hypothesis:

ii) Consequently, increased local ambient temperatures or additional water provided by pre-eruption volcanic activity (e.g., volcanic degassing) may have supported tree growth causing the NDVI anomaly along the locally confined fissure line.

➔ to be REJECTED

Implications

- Tree growth on Mt. Etna is influenced by factors other than climate.

Chapter 2 "*Tree growth reveals the development of the 1974 Mt. Etna eruption*"

RQ 2) How can tree rings be used to better understand the development of the 1974 flank eruption on Mt. Etna? ➔ Manuscript 2

Based on the research findings presented below this second research question can be answered with **YES.**

Analyzing tree-ring width of trees growing along the 1974 eruptive fissure, the consequent results revealed low climate correlations between tree-ring chronologies and climate variability in agreement with our extensive climate analyses of chapter 1. Further, we did not find any significant changes in tree-ring width before the flank eruption of 1974. In contrast, we found a significant depression in tree-ring width in 1975 and 1976, two consecutive years immediately following the flank eruption.

Based on our findings, showing that tree rings were not particularly narrow or wide before the eruption, we showed that tree growth was not affected by pre-eruption activity. Therefore, we conclude that the pre-eruption activity must have started towards the end or after the 1974 vegetation season when tree-ring formation was already completed but photosynthesis was still active and was influenced by the volcanic activity resulting in the reduced NIR anomaly (De Carolis et al., 1976).

Therefore, we can reject our third hypothesis:

iii) Because the NIR anomaly caused by the pre-eruption phase was a momentary measurement in September 1973 we do not know how long this phase lasted. If it took place over an extended time period, there must be an effect on trees growing in the that area. This effect would, as a consequence, be visible in tree rings.

➔ to be REJECTED

Compared to other eruptions (e.g., Houlié et al., 2006) this finding suggests a short pre-eruption activity related to a reportedly fast magma ascent (Armienti et al., 1988).

We successfully demonstrated that tree rings can be used to better understand the development of flank eruptions and the duration of pre-eruption periods.

We can consequently accept our fourth hypothesis:

iv) Therefore, tree rings may provide better understanding of eruption developments.
➔ to be ACCEPTED

Additionally to our research questions we found evidence of strongly reduced, sometimes inexistent tree growth immediately following the 1974 flank eruption for a duration of two years. As a consequence, tree rings could be used to correctly date historic flank eruptions where the time of eruption is unknown and cannot be reconstructed otherwise.

v) Further, tree-ring chronologies can be used to date past volcanic flank eruptions.
➔ to be ACCEPTED

Implications

- Tree-ring analysis can be used to better understand pre-eruption activity and eruption development.
- Tree rings are a useful tool to date currently undated flank eruptions.

Chapter 3 *"Carbon and oxygen isotopic indicators of pre- and post-effects of volcanic eruptions in tree rings on Mt. Etna (Italy)"*

RQ 3) Are carbon and oxygen stable isotopes and radiocarbon in tree rings influenced by volcanic activity before and during the 2002/2003 eruption?
➔ Manuscript 3

Based on the research findings presented below this second research question can be answered with **YES.**

Carbon and oxygen stable isotope ratios in tree rings of trees growing along the 2002/2003 eruptive fissure on Mt. Etna are influenced by temperature and precipitation during summer. Except for the 2003 tree-growth season immediately following the eruption event, where carbon and especially oxygen stable isotope ratios are strongly reduced, mixed effect climate models are able to explain a large portion of the stable isotope variabilities.

Therefore, we conclude that stable isotope ratios (carbon and oxygen) in tree rings from trees growing along the 2002/2003 eruptive fissure were influenced by the ongoing volcanic activity. We suggest that the reduced signatures of both isotopes during the eruption was caused by the uptake of water from a source other than precipitation or surface water (e.g., degassing water vapor).

These findings allow to accept our fifth hypothesis:

vi) Trees have captured changes in stable isotopic ratios of carbon and oxygen induced by pre-eruption volcanic activity preceding the 1974 Monte de Fiore eruption.
➔ to be ACCEPTED

Between the growth seasons of 1992 and 2000 the ^{14}C content analyzed from tree-ring cellulose very well reflects the atmospheric ^{14}C content. In contrast, some of the measurements in 2001 and 2002, the two growth seasons prior to the surface eruption, revealed strongly reduced ^{14}C contents.

This reduction very well coincides with the NDVI anomaly (Houlié et al., 2006). Therefore, despite some ambiguity in the radiocarbon measurements before the eruption

our results suggest that trees may indeed have taken up ^{14}C depleted CO_2 from pre-eruption volcanic degassing. CO_2 fertilization induced by pre-eruption volcanic activity could, therefore, be the main reason for the NDVI anomaly.
Based on these findings we can label our sixth hypothesis as "probable":

vii)	Trees have taken up increased levels of CO_2 from volcanic gasses before the eruption leading to reduced values of ^{14}C in tree rings. ➔ "PROBABLE"

Implications

- Along volcanic fissures volcanic activity can influence stable oxygen ratios in tree rings allowing to detect changes in water sources.
- Likely depending on the amount of volcanic degassing expelled radiocarbon may lead to fertilization or poisoning effects resulting in positive / negative influence on trees, as previously introduced, which could assess pre-eruption activity using NDVI measurements derived from satellite imagery.

Overall conclusion

Highlighting changes in tree growth parameters related to volcanic precursor activity and surface eruptions this thesis shows that the NDVI anomaly depicting increased photosynthesis along the 2002/2003 eruptive fissure was not induced by water availability or changes in ambient temperature (Manuscript I).

Nevertheless, the results reveal a potential influence of pre-eruption CO_2 degassing, which reduced the ^{14}C content of tree-ring material. Additionally, a strong depletion of $\delta^{18}O$ within the tree-ring material proves the uptake of volcanic groundwater by the trees.

Therefore, the thesis presents proof that the NDVI anomaly was caused by volcanic activity likely related to pre-eruption degassing (Manuscript III).

In contrast, the 1974 pre-eruption NIR anomaly depicting vegetation activity could not be supported by any evident anomaly in tree-ring width before the surface eruption. However, there was a strong tree-ring width signal after the eruption. This led to the conclusion that the appearance of the pre-eruption NIR signal was too short to influence tree-ring width but tree rings can very well be used to date currently undated flank eruptions.

Therefore, the thesis provides evidence that trees can and should be used as archives to date past events and to derive information on the speed of shallow surface magma intrusion before surface eruptions (Manuscript II).

Outlook and Perspectives

Threats imposed by volcanoes worldwide are expected to continue in the future. Therefore, the improvement of early warning systems is of great importance. Our interdisciplinary study extended our knowledge about volcanic eruptions and their impact on tree growth and physiology. Combining insights from multiple disciplines such as geophysics, geochemistry, volcanology, petrology, remote sensing and dendrochronology enabled us to jointly interpret effects towards a deeper understanding of pre-eruption activity and its influence on the vegetation. We opened a new research avenue which promises to largely improve assessment of volcanic hazards in the future.

In this project we applied dendrochronological methods as a tool to improve our understanding of the influence of pre-eruption volcanic activity on tree growth on Mt. Etna. The pioneering character of this investigation not only revealed the nature of volcanic influence on trees, but also demonstrated the suitability of applying tree-ring research to answer volcanological research questions promoting an interdisciplinary approach towards a better understanding the broader impact of volcanic activity on the environment.

Having analyzed the influence of climate variability on tree growth, tree-ring width and isotopic ratios in tree rings, this project lead to the main findings summarized below.

1 Relevance

- Tree growth on Mt. Etna is influenced by several regional factors other than precipitation and temperature. These factors may be on one hand related to local site-specific stand conditions, such as exposition, topography, competition or nutrient availability, and disturbances, such as wildfires, and on the other hand to volcanic activity.
- Tree-ring analysis of trees growing along eruptive fissures, which can be influenced by volcanic activity prior and during the eruption can be applied to better understand pre-eruption activity and eruption development. If the time of volcanic activity overlaps with the vegetation season and if the activity is of enough length, the tree-ring physical and chemical characteristics may be affected to such an extent that they can provide currently unexplored insights into the development of past eruptions. In

contrast, during short-term sudden eruptions, the overlap with the vegetation season is only short or inexistent. Accordingly, trees are affected during but not necessarily before the eruption. Therefore, in such cases tree-ring chronologies can be used to assess the onset of an eruption as well as to reconstruct eruption years of currently undated flank eruption.

- Along eruptive fissures volcanic activity can influence the stable oxygen isotopic composition in tree rings because of changes in water sources. Tree-ring stable oxygen isotopic analyses may, therefore, allow the detection of water uptake by trees from different, deeper water sources, such as those associated with magma arising before eruptions.
- Pre-eruption degassing radiocarbon-depleted carbon dioxide may lead to fertilization effects resulting in positive influence on tree photosynthesis, which can be detected using NDVI measurements derived from satellite imagery. This observation implies that remote sensing may be used to predict and constrain time and location of volcanic flank eruptions occurring close to forest stands (Figure 10).

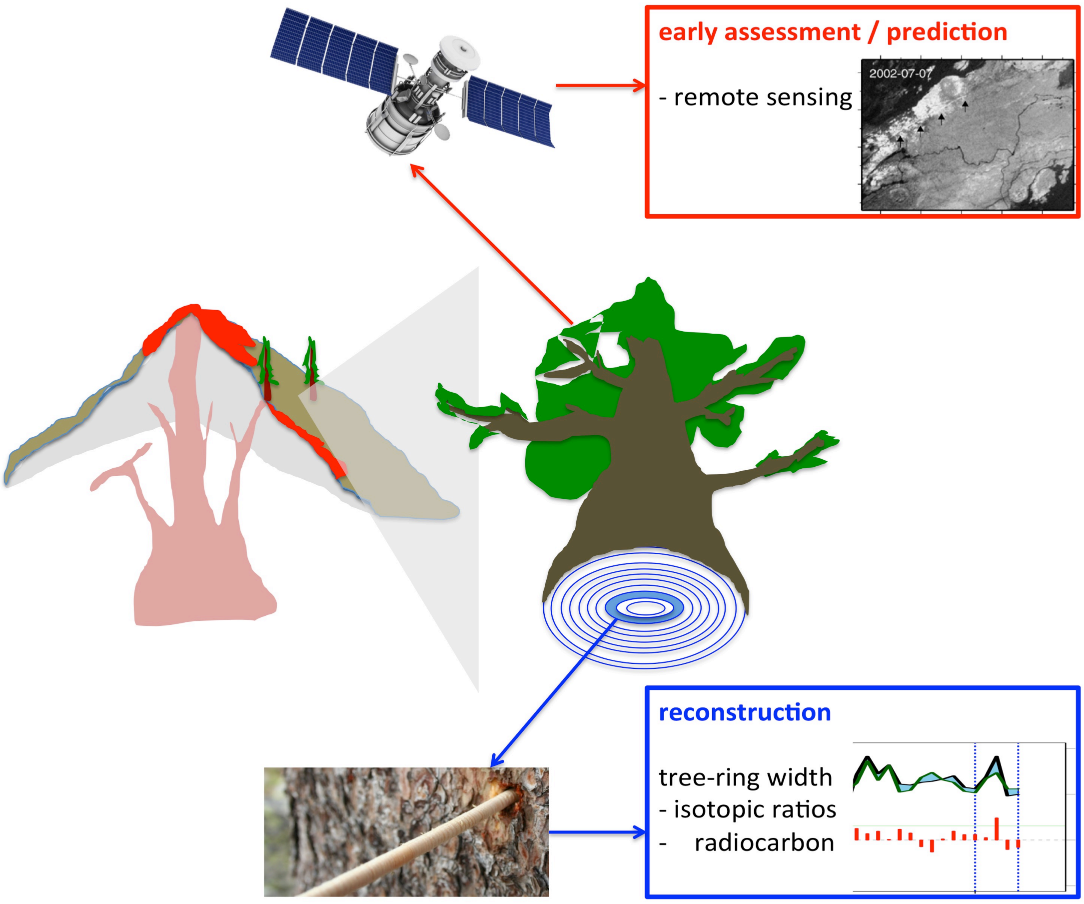

Figure 10 *Potential of trees for early assessment (red) and reconstruction (blue) of volcanic flank eruptions.*

2 Open aspects

Despite having provided a deeper understanding of the interactions between pre-eruption activity and tree-growth ring parameters this study stimulates further investigation on the following research questions.

- It appears that different eruption types affect tree growth differently. While the 1974 eruption with its fast propagation and short pre-eruption activity did not affect tree-ring width, the 2002/2003 eruption resulted in a long term (two years) NDVI anomaly prior to eruption. How does pre-eruption activity of different eruption types (e.g., explosive and effusive) affect vegetation?

- Our ^{14}C results suggest that the enhanced NDVI signal may have been caused by CO_2 fertilization induced by pre-eruption activity. Continuing research on tree rings from additional flank eruptions on Mt. Etna or on further volcanoes could help in strengthening this observation.

- Finally, fertilizing elements, such as phosphorus provided by pre-eruption activity should be studied towards their beneficial effects on trees.

3 Importance of trees as a proxy

The value of tree rings as an archive containing information on the history of volcanic activity lies in the annual conservation of a variety of environmental information (including ring width, isotope ratios and radiocarbon), which remain unaltered after completion of ring formation. Similar natural archives (e.g., ice cores) also provide valuable information but can only tell us about large-scale eruptions and its effects after the event. Trees can tell us what happened prior to eruption.

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Part B: Appendix

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Curriculum Vitae

RUEDI SEILER

OrcID: orcid.org/0000-0003-3293-6981
MSc Geography

Research Group "Dendroecology"
WSL Swiss Federal Institute for Forest, Snow and Landscape Research
CH-8903 Birmensdorf
Switzerland
e-mail: ruedi.seiler @wsl.ch

Birth: St. Gallen, Switzerland, 17 January 1984
Citizenship: Swiss

Research

PhD student	*Swiss Federal Institute for Forest, Snow and Landscape Research WSL*, Birmensdorf (Switzerland), 04/2013 - present PhD-project: *"Tree growth rings as early indicators of volcanic activity on Mt. Etna (Italy)"* Thesis Advisor: Dr. Paolo Cherubini (WSL) - Scientific writing and presentation - Teaching at university level

Education

MSc in Geography	*University of Zurich* (Switzerland) Thesis Advisor: Prof. Dr. Markus Egli (UZH) 08/2008 - 10/2010
BSc in Geography	*University of Zurich* (Switzerland) Thesis Advisor: Prof. Dr. Max Maisch (UZH) 08/2005 - 07/2008

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On the potential of alpine lakewood for Geochronology, presentation at WSL, HS 2015

Swiss alpine lakewood - a new approach to climate reconstruction using dendrochronological methods. Presentation at UZH, FS 2015

Tree rings and volcanic eruptions, presentation at UZH, HS 2014

Climate change and the oceans - sea level, temperature, salinity, circulation and biochemistry. Presentation at UZH, FS 2014

Increased tree-ring growth prior to volcanic eruptions. Presentation at the Geochronology Summer School, Bergün 2013

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RESEARCH ARTICLE

Insensitivity of Tree-Ring Growth to Temperature and Precipitation Sharpens the Puzzle of Enhanced Pre-Eruption NDVI on Mt. Etna (Italy)

Ruedi Seiler[1,2☯]*, **James W. Kirchner**[1,3☯], **Paul J. Krusic**[4,5‡], **Roberto Tognetti**[6‡], **Nicolas Houlié**[7‡], **Daniele Andronico**[8‡], **Sebastiano Cullotta**[9†‡], **Markus Egli**[2‡], **Rosanne D'Arrigo**[10‡], **Paolo Cherubini**[1,2,10☯]

1 Swiss Federal Institute for Forest, Snow and Landscape Research WSL, Birmensdorf, Switzerland, **2** Department of Geography, University of Zurich, Zürich, Switzerland, **3** Department of Environmental Systems Science, ETH Zurich, Zürich, Switzerland, **4** Navarino Environmental Observatory, Messinia, Greece, **5** Institutionen för Naturgeografi, Stockholm University, Sweden, **6** Dipartimento di Bioscienze e territorio, Università del Molise, Contrada Fonte Lappone, Pesche, Italy, **7** Department of Earth Sciences, ETH Zurich, Zürich, Switzerland, **8** Osservatorio Etneo, INGV, Sezione di Catania, Italy, **9** Università di Palermo, Palermo, Italy, **10** Lamont-Doherty Earth Observatory, Palisades, New York, United States of America

☯ These authors contributed equally to this work.
† Deceased.
‡ These authors also contributed equally to this work.
* ruedi.seiler@wsl.ch

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Abstract

On Mt. Etna (Italy), an enhanced Normalized Difference in Vegetation Index (NDVI) signature was detected in the summers of 2001 and 2002 along a distinct line where, in November 2002, a flank eruption subsequently occurred. These observations suggest that pre-eruptive volcanic activity may have enhanced photosynthesis along the future eruptive fissure. If a direct relation between NDVI and future volcanic eruptions could be established, it would provide a straightforward and low-cost method for early detection of upcoming eruptions. However, it is unclear if, or to what extent, the observed enhancement of NDVI can be attributed to volcanic activity prior to the subsequent eruption. We consequently aimed at determining whether an increase in ambient temperature or additional water availability owing to the rise of magma and degassing of water vapour prior to the eruption could have increased photosynthesis of Mt. Etna's trees. Using dendro-climatic analyses we quantified the sensitivity of tree ring widths to temperature and precipitation at high elevation stands on Mt. Etna. Our findings suggest that tree growth at high elevation on Mt. Etna is weakly influenced by climate, and that neither an increase in water availability nor an increase in temperature induced by pre-eruptive activity is a plausible mechanism for enhanced photosynthesis before the 2002/2003 flank eruption. Our findings thus imply that other, yet unknown, factors must be sought as causes of the pre-eruption enhancement of NDVI on Mt. Etna.

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Introduction

Early detection of precursors to volcanic eruptions is important in preventing major damage and loss of life. To date, these precursors have mainly included seismic, geochemical, petrographic, ground deformation and gravimetric changes that are used to assess volcanic activity shortly before eruptions (e.g., [1–6]). Surface deformation, small earthquakes, and release of volcanic gases are typically triggered by the ascent of magma in volcanoes [7]. Volcanic monitoring by remote sensing includes the acquisition of different geochemical and geophysical parameters which record volcanic processes, such as gas emissions and hydrological variations, over time (e.g., [8–10]). Using remote sensing data, an increased Normalized Difference Vegetation Index (NDVI) was observed along subsequent eruptive fissures on Mt. Nyiragongo (Congo) and Mt. Etna (Italy), as early as two years prior to eruptions of both volcanoes [11]. NDVI is closely associated with the amount of photosynthetically active radiation intercepted by vegetation, and thus with both the spatial coverage of green biomass and the chlorophyll content in leaves [12,13]. On Mt. Etna, the enhanced NDVI signal [11] was detected along a narrow line on the northeastern flank; this line later developed into an eruptive fissure during the 2002/2003 flank eruption, suggesting that enhanced photosynthesis may be related to a coming volcanic eruption.

The observed NDVI signal raises the question of whether, and how, eruptive precursor activity could influence photosynthetic rates. A comparison of tree growth with environmental parameters is necessary to estimate their influence on tree growth and to assess the potential contribution from volcanic activity. Increased photosynthesis may be induced by a number of environmental factors that are affected by pre-eruptive volcanic processes, but the most probable are an increase in heat or water availability associated with volcanic degassing (e.g., [14–16]).

Trees in temperate climates form annual growth rings, and variations in their tree-ring characteristics (width and density) reflect changes in the environmental conditions in which they grow. At high elevations and high latitudes, where the limiting factor is summer air temperature, tree growth is typically enhanced during warm summers (e.g., [17,18]). Conversely, in semi-arid ecosystems, such as in Mediterranean lowlands, growth is primarily regulated by precipitation and is enhanced during wet years [19,20]. Consequently, tree rings, often used as indicators of photosynthetic rates [21], also serve as useful proxies for climate [22,23].

The Mediterranean region is characterized by hot and dry summers and mild, humid winters [24,25]. Maximum rainfall occurs predominantly in autumn and sometimes during winter [26]. Precipitation minima and temperature maxima coincide with the period of most intense solar radiation, limiting water availability during the summer season (e.g., [27]). High rainfall variability over the year greatly affects drought severity and hampers growth [28]. Rainfall during spring is the most important factor influencing tree growth and vegetation activity of Mediterranen forests, particularly at more xeric, low-elevation sites, as also shown by remote-sensing-based model simulations and tree-ring-based growth analyses [29]. In more temperate high-elevation conditions, drought often has a minor impact on tree growth because precipitation is less limiting. In the high-elevation forests on Mt. Etna where the increased NDVI prior to the eruption was detected [11], tree growth might be enhanced by increased air temperature during the vegetation period or, given the southern latitude, by increased water availability.

Here we analyse the relationships between ring-width indices of *Pinus nigra* J.F. Arnold and monthly precipitation and air temperature, and compare our ring-width series from Mt. Etna with series from trees growing at similar elevations in Calabria, a region located at a similar latitude on the Italian peninsula without the direct influence of volcanic activity. Our hypotheses are that i) ascending magma led to an increase in local ambient air and soil temperature which positively influenced photosynthesis rates and tree growth, and that ii) water vapour from volcanic degassing locally provided additional humidity/moisture/water which became available to trees influencing photosynthesis rates and tree growth. To address these issues we assess to what extent tree-ring growth at the highest elevations on Mt. Etna is influenced by climate, i.e. air temperature and precipitation, to indirectly determine i) whether an increase in temperature caused by an incipient volcanic eruption (e.g., [30,14]) would likely induce higher photosynthetic productivity, and ii) whether, at specific locations close to rift zones, additional water availability induced by degassing of water vapour associated with the rise of magma prior to an eruption (water is the most abundant component in volcanic gas, [16]) would likely increase the photosynthetic capacity of Mt. Etna's trees (see [11]).

Materials and Methods

Study area

Mt. Etna is a stratovolcano situated in the northeastern part of Sicily. With an area of approximately 1600 km^2 and a summit elevation of roughly 3330 m a.s.l., Mt. Etna is an isolated high mountain exposed to air masses from the Mediterranean Sea. The climate on Mt. Etna is strongly maritime on the eastern flank [31,32], with drier conditions on its western flank [33]. The slopes are characterized by lava flows of different ages [34]. Most of the lower elevations, being especially fertile, have been settled and used for agriculture for thousands of years. The higher elevations, from 1000–1600 m a.s.l., are dominated by European beech (*Fagus sylvatica* L.), and from 1600 m to treeline (~2000 m a.s.l.) by Corsican black pine (*P. nigra*). Though the treeline climatically determined at such latitudes would otherwise be higher [35,36], eruption-induced wildfires and the lack of soils on lava flows hinder its uphill development [37–39].

Besides volcanic eruptions and lava flows on Mt. Etna, other volcanic processes, such as degassing through small vents, are also present but difficult to quantify [40]. The soils of Mt. Etna are primarily classified as Regosols, Eutric or Dystric Cambisols and (Mollic) Andosols. The characteristics of these soils predominantly depend on the surface age of the lava flow and volcanic deposits from which they have developed [38,41,42]. In general, soils at intermediate to high elevation on Mt. Etna (i.e. above 800 m a.s.l.) are mostly described as Andisols with a sandy loam texture, vitric characteristics, an udic moisture regime [39] and good water holding capacity [43]. However, less mature, young soils on fresh lava flows may be less developed resulting in lower water holding capacity.

The forests around the flanks of Mt. Etna are greatly affected by both natural and anthropogenic disturbances, such as wildfires, lava flows, avalanches and logging. At the lowest elevations, from the plains up to 900 m a.s.l., agricultural crops and orchards, e.g., orange, lemon, almond, pistachio, and chestnut, are found. Only a few forest stands, mainly at the highest elevations on the northern or northeastern side of the mountain, are undisturbed [31]. Meteorological station data from Linguaglossa (530 m a.s.l., 15°08'42" E, 37°50'27" N, timespan: 1893–2004) based on daily temperatures and precipitation measurements give an average annual temperature of 18°C and a total annual precipitation of 1400 mm. Additionally, monthly temperature averages in winter are above zero at at all stations.

Sampling

In total, we sampled 143 trees (*P. nigra*), with permission issued by the local forest authorities (Corpo Forestale della Regione Siciliana, Distaccamento di Bronte, Piazza Cadorna 11, I-95034 Bronte, Catania, Italy), at four high-elevation (1500 to 1900 m a.s.l.) forest sites on the northeastern and western slopes of Mt. Etna (Fig 1): 52 trees growing close to the 2002/2003 eruptive fissure (Group 1), 27 trees growing close to the 1928 eruptive fissure (Group 2),

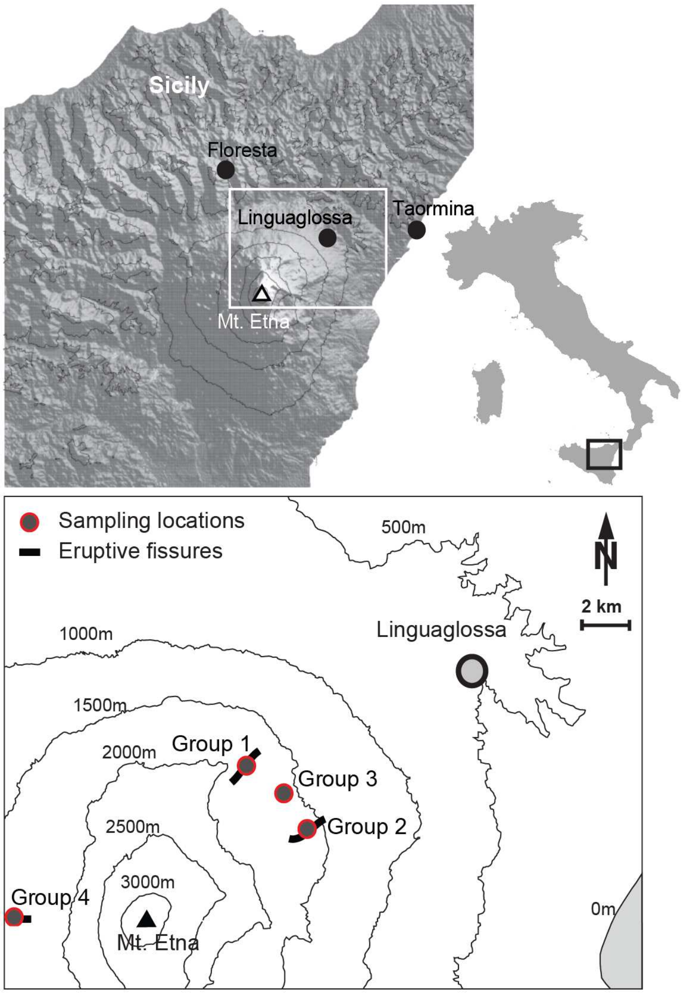

Fig 1. Map of sample locations. Mt. Etna sample sites (Group 1–4) on the northeastern and western slopes at an elevation range from 1600 to 1850 m a.s.l. indicating the location where samples were taken and the location of the meteorological stations. The NDVI anomaly overlays with the 2002 fissure line. A more detailed map can be found in Houlié et al. (2006). The map of Italy was created using the program R (Version 3.1.3; URL: http://www.R-project.org/) [45], the topographic map showing Sicily was created using Generic Mapping Tools (Version 5.2.1; URL: http://gmt.soest.hawaii.edu/) [46] and the basis map was taken from Egli et al. (2007) [47].

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38 trees growing in the same elevation band but far from any obvious fissures (Group 3), and 26 trees growing close to the 1974 eruptive fissure (Group 4). All sites are dominated by *P. nigra* and *Fagus silvatica* and are located at a comparable elevation and slope with NNE aspect except for group 4, which is located on the western flank on a western-aspect slope. Apart from that, there were no evident differences between the four sites in terms of forest-stand density, composition of tree species, topography and slope (about 14%). From each tree, two 0.5 cm diameter cores were taken orthogonally with respect to each other using a corer with a three-threaded auger by Haglof (Haglof Inc., Sweden), wrapped in paper and transported to the laboratory. All samples were mounted on wooden supports and cut using a microtome at an angle of roughly 30° to the radial axis of the tree to prevent core breakage

[44]. For later comparisons, three ring-width chronologies, located close to Mt. Etna, derived from coniferous trees uninfluenced by Mt. Etna growing at similarly high elevations in Calabria (Gambarie, Monte Pollino and Sierra da Crispo) were retrieved from the International Tree-Ring Databank (ITRDB, NOAA, U.S.A.)

Ring-width measurements

All ring widths were measured to the nearest 0.01 mm using a Leica Wild M32 binocular microscope (Leica, Germany) with 25-50x magnification, coupled to a LINTAB measuring table and computer with TSAPwin (Time Series Analysis Program) software (RinnTech, Heidelberg, Germany). Core measurements were visually crossdated against each other and any inconsistencies, if found, were eliminated. Subsequent crossdating of the single-tree chronologies with their respective mean site chronology by visual and statistical measures was performed using TSAPwin and COFECHA (50-year segments with a 25-year overlap) [48,49]. Since the sampling dates of all trees were known, crossdating was primarily used to ensure that prominent tree-ring patterns were not shifted between trees and no rings were missing.

Meteorological data

We used monthly precipitation and air temperature data recorded at three meteorological stations on Mt. Etna: Floresta (1275 m a.s.l., 14˚54'31" E, 37˚59'15" N, Timespan: 1924–2004), Linguaglossa (530 m a.s.l., 15˚08'42" E, 37˚50'27" N, Timespan: 1893–2004) and Taormina (248 m a.s.l., 15˚17'34" E, 37˚17'34" N, Timespan: 1906–2004). Although longer records are available for Linguaglossa and Taormina, we only used data from 1924–2004 at all three sites so that they could be compared over a common period. In addition, interpolated monthly temperature, precipitation, cloud cover and Palmer Drought Severity Index (PDSI) data for the Mt. Etna region and Calabria from the Climatic Research Unit, University of East Anglia, Norwich, U.K. (CRU) [50] were compared to the above-mentioned station data and the tree-ring data [51,52]. Opposed to temperature and precipitation data, the PDSI incorporates both temperature and precipitation, representing long-term drought taking prior months' condition into account. On the other hand, delayed water runoff from snow during spring is not accounted for in the index (e.g., [53]). Correlations between the data recorded at the meteorological stations and the interpolated datasets were calculated, to assess whether the interpolated data could be used to further analyse relationships between climate and tree growth.

Data analysis

All raw measurement series were standardized using the program ARSTAN (http://www.ldeo.columbia.edu/tree-ring-laboratory) by applying 30-year spline detrending combined with a variance stabilization, to remove the age trend and produce detrended ring-width indices [48,54]. All chronologies were used individually to analyse the relationships between climate and growth at different sampling sites.

We performed correlation analysis and response function modelling to quantify the influence of climate on tree growth [55]. We tested the statistical significance of temperature, precipitation, cloud cover and Palmer Drought Severity Index (PDSI; e.g., [56,57]) in different months and seasonal combinations of monthly values, including prior-year values, using Spearman rank correlation. Linear regression, as described by [58], was used to remove long-term trends in the meteorological data and avoid artificially inflating correlation values. Based on results from simple Spearman rank correlations between all the Mt. Etna chronologies and monthly meteorological data, we built "Visual Regression Models" (VRM) which were defined as standard multiple linear regression models including statistically significant ($p < 0.05$) monthly variables or monthly groupings.

In addition to VRM, Stepwise Linear Regression Modelling (SLRM), based on the Akaike Information Criterion (AIC) and using a forward-backward approach [59], was used to identify those climate variables that explained the greatest variance in each chronology on Mt. Etna. The SLRMs were based on monthly variables and groupings that defined the spring and summer seasons. For all models we only used variables that did not overlap in time (e.g., precipitation in May and precipitation in spring would not be used together because both contain May precipitation values).

The models (SLRM) were tested for collinearity among explanatory variables using variance inflation factor (VIF) analysis [60]. VIF values were all lower than 4, implying a lack of strong collinearity among explanatory variables [61]. This led to selecting the final climate models based on the AIC.

We compared how well the two model types (VRM and SLRM) explained the climate—ring width relationship:

1. Qualitative differences between the two model types included differences in monthly parameters used in the models.
2. Quantitative differences, comparing adjusted-R^2, show the increase/decrease of explanatory power from one model type to another.

To test the reliability of the models, as well as the degree of overfitting due to including too many variables during the stepwise model selection process, we divided the timespan covered by both meteorological and ring-width measurements at Mt. Etna (1924–2004) and Calabria (1924–1980) into two segments [62,63]. The models were run on both segments to compare differences over time. In addition, the two segments were used for both forward- and backward validation to quantify model robustness over time [53].

On Mt. Etna, forward validation used a model based on the time segment 1925–1964 to predict tree growth during 1965–2004, and backward validation used a model based on the later time segment to reconstruct 1925–1964 tree growth. For the Calabria chronologies we used the same validation procedure based on the two time segments from 1925–1951 and 1952–1980. AIC was used to test for overfitting.

We calculated how the explanatory power (R^2) varied through time by applying our SLRMs to a 15-year moving window with 14 years overlap to identify periods of higher and lower correlations between ring-width and our climate models [52].

Results

The Mt. Etna chronologies show higher variability in their ring-width patterns than the chronologies from Calabria (Fig 2). The four raw ring-width chronologies (Group1-4) from Mt. Etna display growth patterns that are strongly influenced by the establishment of new generations of trees. Young trees, most germinating after 1950, greatly increase the mean ring-width, producing a clear age trend (Fig 2). Tree age ranges from 55 to 122 years on Mt. Etna, and from 128 to 299 years in Calabria. Descriptive chronology statistics are given in Table 1.

The monthly meteorological data show stronger inter-station correlations for air temperature (Spearman correlation coefficients up to $r = 0.86$; $p < 0.01$) than for precipitation (up to $r = 0.83$; $p < 0.01$), as usually reported in the literature (e.g., [51,64]). In addition, we find that instrumental station data also correlates significantly with the interpolated CRU data (highest Spearman $r = 0.67$ to 0.87 for temperature; $r = 0.67$ to 0.78 for precipitation; $p < 0.01$). Given

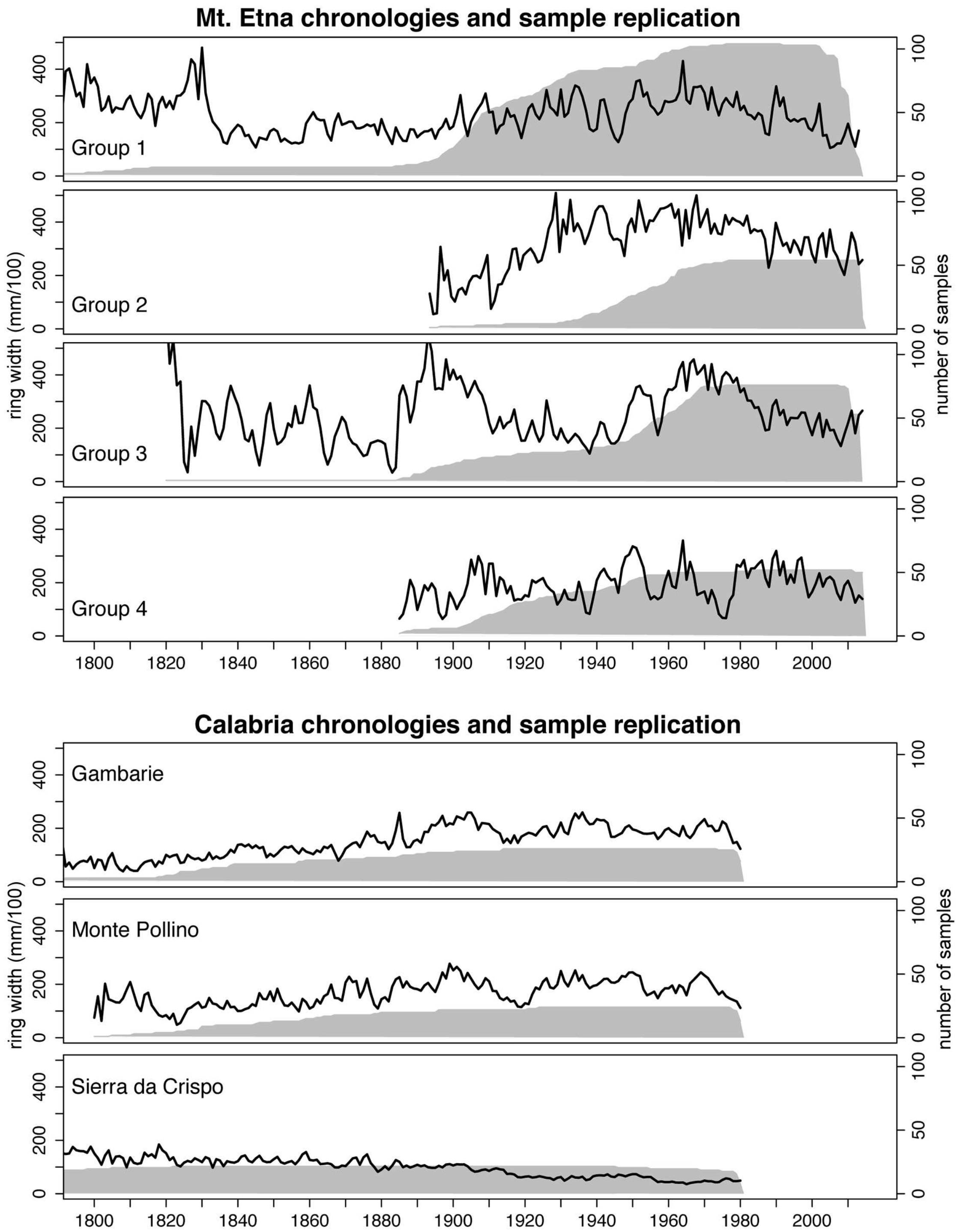

Fig 2. Chronologies and sample replication. Average chronologies (black lines) and sample replication of all samples (grey area) of Mt. Etna (Group 1–4) and Calabria (Gambarie, Monte Pollino and Sierra da Crispo.

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Table 1. Sample overview information. Descriptive statistics of sample chronologies (Group 1–4) from Mt. Etna, and the chronologies from Calabria (Gambarie, Monte Pollino and Sierra da Crispo) displaying number of series (core-series), total length (years) of group chronologies, series intercorrelation (measure of common growth signal in the chronology), mean sample length (years), elevation (m a.s.l.) and species.

		no. of series	total length	ser.interc.	mean length	elevation	species
Mt. Etna	Group 1	104	229	0.498	97	1850	*Pinus nigra*
	Group 2	54	121	0.577	67.1	1700	*Pinus nigra*
	Group 3	76	195	0.529	82.7	1600	*Pinus nigra*
	Group 4	52	130	0.597	95	1670	*Pinus nigra*
Calabria	Gambarie	26	191	0.344	130.7	1850	*Abies alba*
	Monte Pollino	24	181	0.403	128.2	1720	*Ablies alba*
	Sierra da Crispo	22	540	0.421	299.1	2000	*Pinus leucodermis*

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these correlations, comparable to those found in previous studies [51], we used the interpolated data to assess the climate influence on tree growth.

In general, total summer precipitation produces similarly high correlation values with tree growth as single monthly variables in the same season. Average spring and summer temperature and total spring precipitation produce generally lower correlations than single months during the same season (Table 2). Prior-year precipitation and temperature were also considered but results are not reported because the current year's correlations are higher. Cloud coverage is not significantly correlated with tree growth. In contrast to all other sites, tree growth at Group 3 exhibits a significant negative correlation with PDSI from April to December (results not shown).

In Calabria the Gambarie chronology is primarily sensitive to summer temperature and summer precipitation (Table 2). The Monte Pollino chronology responds more to spring temperatures as well as spring and summer precipitation, and the chronology from Sierra da Crispo is not significantly correlated with any climate variables. The Mt. Etna chronologies correlate with spring and summer temperatures (Groups 1–3), as well as spring and summer precipitation (Groups 1 and 3). Group 4 has no significant correlations with climate. Over all months and seasons the Mt. Etna (Groups 1–4) chronologies are, on average, less strongly correlated with temperature and precipitation than the Calabria chronologies are. The difference in the (absolute value) strength of the correlations between Mt. Etna and Calabria was not, however, statistically significant (Student *t*-test).

Overall we observe similar responses in the chronologies from Mt. Etna and in those from Calabria (Table 2 and Fig 3). The raw numbers of significant correlations between temperature or precipitation and ring width are broadly similar (20 out of 88, or 23% at Mt. Etna, and 14 out of 66, or 21%, in Calabria).

We used the sign test to evaluate whether the correlations between climate and ring width were positive or negative more often than expected by chance. If we pool both the Mt. Etna and Calabria correlations (Table 2), we see that ring widths are positively correlated with spring temperature (22 of 28 month and site combinations; $p < 0.01$ by the two-tailed sign test), negatively correlated with summer temperature (22 of 28 correlations; $p < 0.01$ by the two-tailed sign test), and positively correlated with summer precipitation (18 of 21 correlations; $p < 0.05$ by the two-tailed sign test), but not significantly correlated with spring precipitation (17 negative correlations out of 28 month and site combinations; $p > 0.05$ by the two-tailed sign test). Thus tree growth in these mountain environments tends to be favoured by warm springs (suggesting that water is not limiting in the springtime) and cool and relatively wet summers.

Table 2. Climate-ring width correlation statistics. Spearman rank correlations between climate variables and detrended ring width from Mt. Etna chronologies (Group 1–4) and from Calabria chronologies (Gambarie, Monte Pollino and Sierra da Crispo), where P = precipitation, T = temperature, tot. = total amount of precipitation, avg. = average temperature, and prior = prior year. Values printed in bold are statistically significant with (* = $p < 0.05$, ** = $p < 0.01$, two-tailed). The significance threshold at Mt. Etna is lower than in Calabria ($r = 0.222$ vs. $r = 0.271$, respectively) because the climate and tree ring records overlap for longer on Mt. Etna than in Calabria (81 vs. 57 years, respectively).

	Mt. Etna				Calabria		
SPEARMAN rank correlations	**Group 1**	**Group 2**	**Group 3**	**Group 4**	**Gambarie**	**Monte Pollino**	**Sierra da Crispo**
T February	0.176	0.189	0.217	0.055	0.209	0.184	0.114
T March	** **0.427**	* **0.265**	** **0.327**	0.197	0.152	0.163	0.018
T April	0.144	-0.109	0.064	0.169	0.148	** **0.490**	0.203
T May	-0.106	-0.213	-0.15	-0.033	-0.018	* **0.271**	0.061
T avg. spring	** **0.337**	0.197	* **0.284**	0.14	0.21	** **0.348**	0.11
T June	0.035	-0.094	-0.004	0.172	* **-0.283**	-0.019	-0.068
T July	-0.158	* **-0.223**	-0.136	0.06	* **-0.296**	-0.068	0.026
T August	** **-0.326**	-0.182	** **-0.397**	-0.032	** **-0.408**	-0.05	-0.131
T September	-0.117	-0.147	-0.198	-0.01	-0.178	0.026	0.117
T avg. summer	-0.172	-0.206	-0.203	0.088	** **-0.375**	-0.07	-0.084
prior P December	-0.16	* **-0.261**	** **-0.304**	-0.028	0.087	0.181	0.111
P January	0.131	-0.095	0.091	0.021	-0.137	-0.018	0.059
prior P winter	0.027	* **-0.251**	-0.078	0.043	0.03	0.184	0.182
P February	-0.048	-0.113	-0.159	-0.125	-0.057	-0.128	0.029
P March	* **-0.279**	-0.151	-0.12	-0.079	-0.007	-0.001	0.044
P April	0.009	0.121	0.15	0.103	-0.22	* **-0.279**	-0.031
P May	0.185	0.088	* **0.227**	0.025	0.209	-0.026	-0.179
P tot. spring	* **-0.228**	-0.104	-0.107	-0.095	-0.19	* **-0.308**	-0.015
P June	0.114	0.03	* **0.236**	-0.117	* **0.279**	0.138	0.076
P July	* **0.279**	0.092	* **0.222**	* **0.225**	* **0.303**	** **0.416**	0.186
P August	0.165	-0.043	0.209	0.09	0.083	0.083	0.136
P tot. summer	* **0.271**	0.09	** **0.346**	0.118	* **0.325**	* **0.314**	0.24

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Comparing the VRM and SLRM modelling results (Table 3), we distinguished between models explaining ring width on Mt. Etna and models explaining ring width in Calabria. SLRM's yielded average R^2 values of 20% (8% to 33%) on Mt. Etna and 26% (13% to 39%) in Calabria, demonstrating that precipitation and temperature are not strongly correlated with tree growth compared to other climatic regions. The regression models include both precipitation and temperature variables from spring and summer. There are, however slight differences between the models (Table 4).

We calculated an average improvement in adjusted R^2 from VRM to SLRM of 5% on Mt. Etna and 8% in Calabria (Table 3; Fig 4).

When comparing VRM and SLRM which were statistically significant ($p < 0.05$), a significant model-improvement ($p < 0.05$) was only obtained with Mt. Etna's Group 1 models. These results show that on Mt. Etna even complex models such as our SLRM are not able to explain tree-growth variability much better, demonstrating that tree growth is further influenced by parameters other than climate which induce additional noise to our ring-width data.

When comparing differences over time by running the SLRMs on both time segments separately, on Mt. Etna only two out of eight model-runs on the two time segments led to significant R^2 values ($p < 0.05$), whereas in Calabria the R^2 in four out of six runs was significant (results not shown).

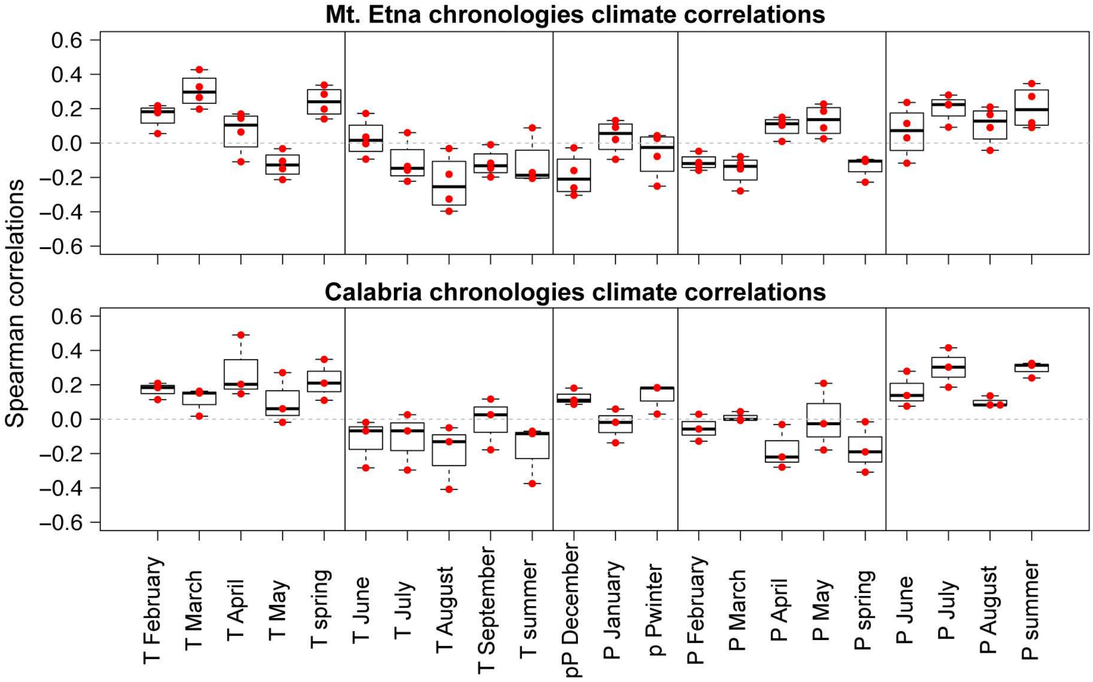

Fig 3. Climate—ring-width correlations. Spearman rank correlation data points of single months and seasonal groupings (red dots) of chronologies from Mt. Etna (top panel) and Calabria (bottom panel) showing the correlation range of each monthly- or seasonal variable with the different group-chronologies; where T = temperature, P = precipitation and p = prior year. Boxplots show the median and lower and upper quartiles, and the whiskers display the minimum and maximum values.

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Mt. Etna model validations demonstrate that the only forward verification resulting in a significant R^2 value ($p < 0.01$) was obtained with the Group 3 model. Forward validation of the Group 1, Group 2 and Group 4 models resulted in statistically non-significant R^2 values. Further, backward validations show that all models calibrated on the second segment show a

Table 3. Statistics of climate models. Overview of model R^2 and adjusted R^2 statistics of the Mt. Etna and Calabria chronology models. Visual Regression Models (VRM) are shown in the left panel, Stepwise Linear Regression Models (SLRM) in the middle panel and the percentage of "model-improvement" from VRM to SLRM is shown in the right panel.

	Visual Regression Models			Stepwise Linear Regression Models			Model improvement (%)	
	R^2	**adj. R^2**	***p-value***	**R^2**	**adj. R^2**	***p-value***	**R^2**	**adj. R^2**
Group 1	0.23	0.19	*<0.01*	0.29	0.24	*<0.01*	6	5
Group 2	0.09	0.04	*0.13*	0.09	0.06	*0.03*	n/a	n/a
Group 3	0.27	0.22	*<0.01*	0.33	0.27	*<0.01*	6	5
Group 4	0	-0.01	*0.96*	0.08	0.06	*0.03*	n/a	n/a
average Mt. Etna	***0.15***	***0.11***	***0.27***	***0.2***	***0.16***	***0.02***	***6***	***5***
Gambarie	0.2	0.17	*<0.01*	0.26	0.23	*<0.01*	6	6
Monte Pollino	0.3	0.24	*<0.01*	0.39	0.34	*<0.01*	9	10
Sierra da Crispo	-	-	-	0.13	0.1	*0.02*	n/a	n/a
average Calabria	***0.25***	***0.2***	***<0.01***	***0.26***	***0.22***	***0.01***	***7.5***	***8***

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Table 4. Model variables used by climate models. Climate variables (single months and seasonal groupings) used in VRM and SLRM models. Monthly variables included in the models are designated as X. Due to time overlaps between single months and seasons, variables that were excluded from the models are designated as e.

		feb	mar	apr	avg.spring	may	jun	jul	aug	avg.summer	dec	jan	tot.winter	feb	mar	apr	tot.spring	may	jun	jul	aug	tot.summer
Group1	VRM		X						X						X					X		
	SLRM		X						X			X					X					X
Group 2	VRM		X					X			X		e									
	SLRM					X					X											
Group 3	VRM		X						X		X							X				X
	SLRM				X	X			X	e	X											X
Group 4	VRM																			X		
	SLRM						X							X								
Gambarie	VRM									X												X
	SLRM			X						X												
Monte Pollino	VRM			X		X										X				X		
	SLRM			X	e						X					X						X
Sierra da Crispo	VRM																					
	SLRM			X																		X

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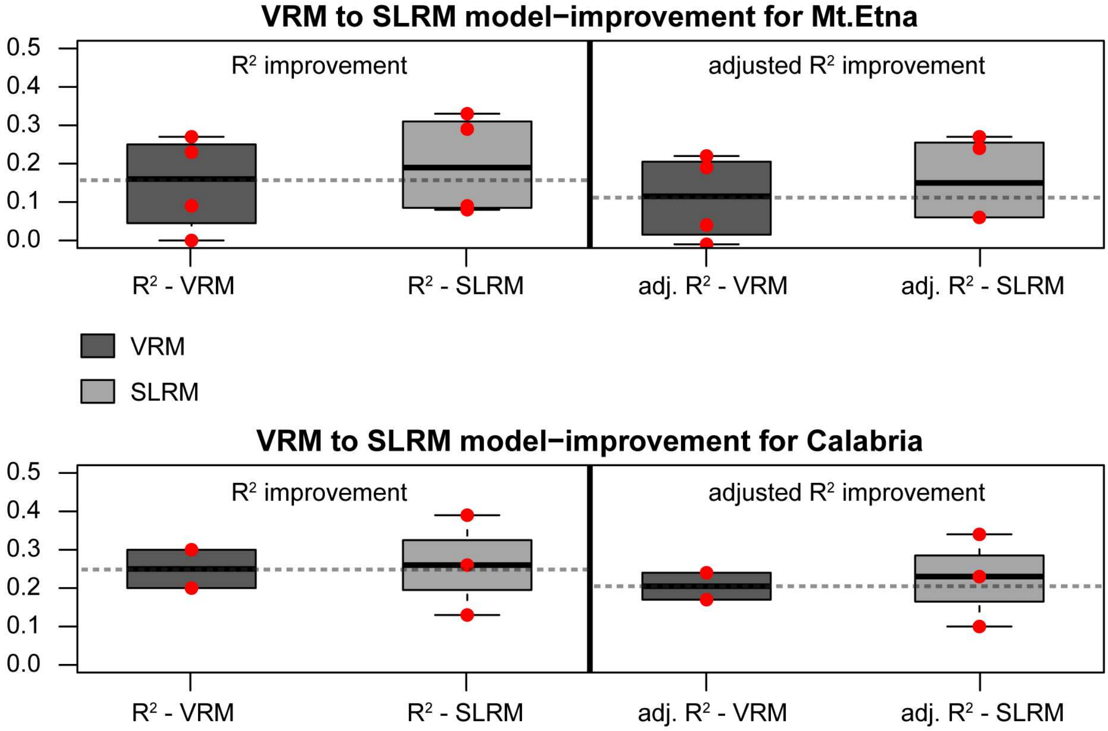

Fig 4. Climate model comparison. Comparisons between individual VRMs (visual regression models) and SLRMs (stepwise linear regression models) revealed only one case (Group 1) where the VRM and the SLRM were both significant ($p < 0.05$) and where a statistically significant model improvement ($p < 0.05$) was calculated. On Mt. Etna, the Group 1 model significantly improved from adjusted $R^2 = 0.19$ (VRM) to adjusted $R^2 = 0.24$ (SLRM). Details are summarized in Table 3.

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decrease to non-significant R^2 values when run on the first segment. Out of eight validation runs (forward and backward) on Mt. Etna only one retained significant R^2 values ($p < 0.01$). Including all validation runs (statistically significant and non-significant), forward validation lost 4% (from an average R^2 of 0.18 in the first period to 0.14 in the second period) and backward validation lost 37% (from an average R^2 of 0.48 in the second period to 0.11 in the first period) of explained ring-width variance on Mt. Etna.

The same calculations for Calabria showed that forward validation (earlier to later time-segment) lost 32% of the explained variance (average R^2 changed from 0.53 to 0.21), while backward validation lost 11% (average R^2 changed from 0.55 to 0.44). We calculated that of all six validation runs (forward and backward) in Calabria, only two backward validations retained significant R^2 values ($p < 0.05$).

These results show that our models (SLRMs) of tree-ring data on Mt. Etna and in Calabria do not withstand the cross-validation test and demonstrate the importance of validating tree-ring based climate models, especially in regions such as the Mediterranean, where climatic factors are not strongly limiting tree growth.

The explanatory power of all models is generally low. The changes in the explanatory power of all models over time are shown in Fig 5. The Mt. Etna models (Groups 1–4) display a wider range of performance with some visual suggestion of a trend of increasing explanatory power over time, while the Calabria models showed less temporal variability.

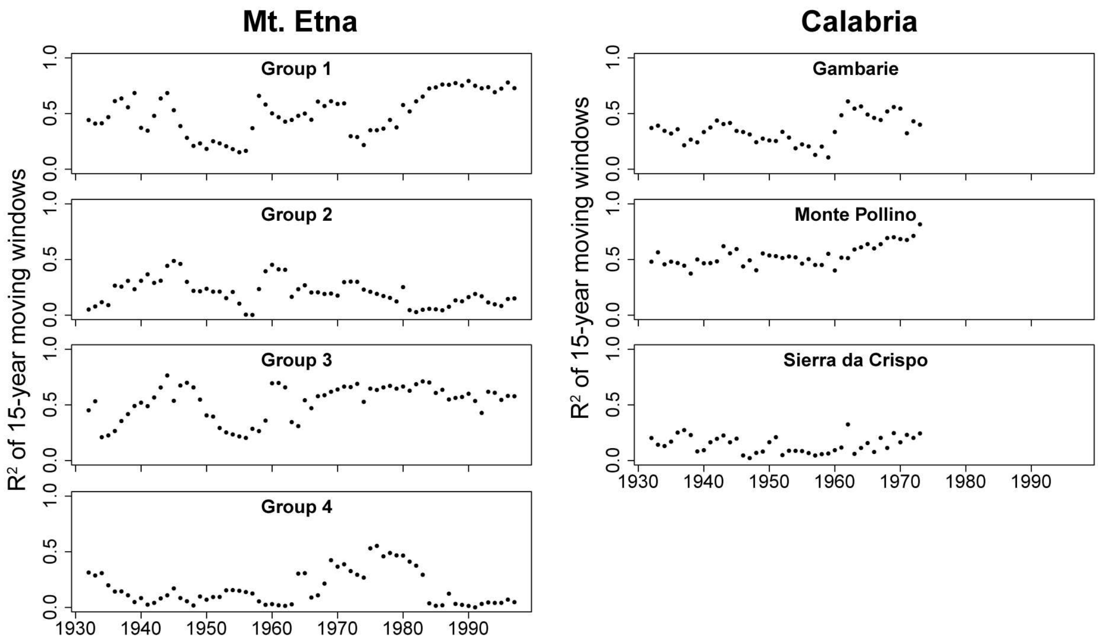

Fig 5. Model strength over time. Change of SLRM model goodness-of-fit statistics for 15-year moving windows over time, showing a visual suggestion of higher temporal consistency among the Calabria models.

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Discussion

In the Mediterranean region, seasonal drought conditions can persist at low elevations for up to five months and have a strong negative impact on tree growth [19,65], whereas at higher elevations precipitation is usually not a limiting factor [e.g., 29]. At the treeline in temperate regions, air temperature is generally the major driver of tree growth, being positively correlated with ring width (e.g., [66–70]). Similar correlations have been observed in the Mediterranean mountains as well [71,72]. At lower elevations, higher temperatures reduce tree growth by increasing evaporative demand and drought stress [73,74]. Our study showed that tree growth at high elevation on Mt. Etna is not much limited by climatic conditions: the correlations between tree-ring width and meteorological data (monthly precipitation, air temperature, PDSI and cloud coverage) were rather weak, suggesting that an increase in local moisture or temperature caused by pre-eruptive volcanic activity was unlikely to have affected tree growth. On Mt. Etna, the correlations between ring width and meteorological data were weaker than in Calabria, suggesting that the tree-ring/climate relationship on Mt. Etna might be affected by other factors. Stepwise linear regression models (SLRM) explained an average adjusted R^2 of 16% of tree growth on Mt. Etna and 22% in Calabria. By comparison, linear regression models using spring to summer temperature at similar elevations in south-western Anatolia explained up to 51% of ring-width variance [75]. Furthermore, climate correlation values on Mt. Etna and in Calabria are lower than those found using response function analyses in the Aegean [76]. Tree-growth response to temperature across the Mediterranean region is complex and strongly affected by the change of environmental factors over longitudinal, latitudinal and elevational gradients [77] and the age of the trees studied [78]. The dependence of tree growth on spring temperature may be reduced at sites that, like Mt. Etna and Calabria, are very close to the sea.

In general, the ring-width chronologies on Mt. Etna showed higher inter-annual variability than those from Calabria, even though the Mt. Etna chronologies were based on greater numbers of trees with a correspondingly greater averaging of random inter-tree variations. Our analyses suggest that non-climatic factors may give rise to a greater variability in tree-ring growth on Mt. Etna than in Calabria. This argument is supported by the larger differences on Mt. Etna between the regression models fitted to the two time periods.

On Mt. Etna, the correlation with summer precipitation (r = 0.27 to 0.35) is lower than in previous studies that found that water is the limiting factor in the Mediterranean region [63,75,76,79–81]. Near treeline on Mt. Etna, which is lower than at other sites at similar latitudes, because not determined by climatic conditions but rather by volcanic activities, other factors, such as higher air humidity with increasing elevation, seem to reduce the influence of summer precipitation on tree growth.

The low correlation values between PDSI and ring width on Mt. Etna (maximum r = 0.29) confirm that moisture availability is not strongly limiting tree growth. Similar results have been reported for *Pinus halepensis* Mill. in Tunisia [82] and for *Pinus sylvestris* L. in south-eastern France [83]. It is notable that *P. nigra* exhibits a drought-avoidance strategy characterized by efficient stomatal control of transpirational water loss [84]. At the same latitudes in Spain, the drought response of *P. nigra* varied along an aridity gradient with the strongest response at the most xeric sites [85]. At comparable latitudes and elevations in Calabria, studies on *F. sylvatica* found no correlations between either water use efficiency or basal area increment and an estimated drought index, suggesting a minimal effect of climate on tree growth during the last century [86], especially when considering the rather udic soil moisture regime at intermediate to high elevations on Mt. Etna [39]. No significant differences in soil properties, such as nitrate and ammonium or phosphorus from soils adjacent to eruptive fissures and soils away from such fissures [87] revealed homogenity of soil characteristics on Mt.Etna and demonstrated that nitrogen (nitrate and ammonium) is unlikely to have induced stronger tree growth.

Due to their high elevation and the subsequent cold, snowy, foggy and humid environmental conditions, the Mt. Etna trees do not appear to be strongly affected by Mediterranean summer drought. The combination of proximity to the sea and high elevation favours persistent seasonal fog and shading by clouds, thus limiting the vapour pressure deficit and reducing water use efficiency [88]. To survive summer droughts, vegetation uses water coming from spring precipitation or, at higher elevation, melting snow, which in some regions can be half of the annual precipitation amount [89]. At the highest elevations on Mt. Etna, winter precipitation is mainly snowfall and, based on our analyses, is not strongly correlated with tree growth (Table 2). The high porosity of the volcanic soils allows rapid infiltration, making a large fraction of the annual precipitation unavailable to the trees, and making it unlikely that winter or spring precipitation could be stored long enough to significantly alleviate summer drought stress.

Significant positive correlations between ring width and spring temperatures were found, except for Group 4. These results confirm those of previous studies on silver fir in southern Italy [52], and in southwestern Anatolia [90]. Based on the positive correlations between March temperatures and ring width on Mt. Etna, high spring temperatures appear to promote an early start of the growing season. Based on the above zero average temperatures during winter measured at all meteorological stations, possible heat discharge from the volcanic fissure in the years before the eruption (e.g., [91]) could not have caused such an early start of the growing season. In contrast, pines are able to photosynthesize during winter; thus mild temperatures in late winter may enhance the availability of reserves (non-structural carbohydrates) for allocation to cambial growth in spring. Mild conditions in spring may stimulate cambial dynamics or induce early cambial reactivation, increasing production of early-wood.

We found negative correlations between ring width and summer temperature, as previously described in Turkey [51,76,92,93], as well as in north-eastern Greece and the Spanish Pyrenees [94]. These correlations may be related to heat waves and the negative effect of drought stress on tree growth. An increase in frequency in hot and dry summers under climate change during the recent past [95] may also increase drought stress indirectly in autumn and further constrain tree growth.

Low climate sensitivity of the studied trees suggests that other factors must have caused the increased pre-eruption NDVI signal. One of the factors which could have induced fertilization is an increased carbon dioxide (CO_2) concentration, which is commonly found in the surrounding of volcanic fissures (e.g., [96,97]).

Pre-eruption CO_2-degassing has been observed on Mt. Etna [98] supporting the possible effects on trees analysed in this study. Even though it has been shown that the deposition of volcanic trace elements in tree rings appears to be unrelated to the occurrence of volcanic events [99] trees have been found to grow faster upon elevated concentration of CO_2 gas in the surrounding atmosphere (e.g., [100,101]), as may be induced by emissions from the volcanic system. Analyses of tree rings have shown that trees close to natural CO_2 springs did take up fossil CO_2 but did not grow faster [102–104]. Depending on the amount of increased CO_2 concentration the effects on tree growth can either be positive [105], negative [106] or even lethal, such as at Mammoth Mountain in California [107]. However, a number of studies have shown that adult, mature trees do not grow faster under elevated CO_2 concentrations [102,108,109]. Therefore, it is not clear if an enhanced CO_2 concentration would be a suitable candidate to explain the increased NDVI.

Conclusions

We conclude that tree growth at the highest elevations on Mt. Etna is not significantly limited by climate. Our samples were taken near Mt Etna's upper treeline, but this treeline is not climatically determined; instead it is defined by volcanic activity and related disturbances such as wildfires. Consequently, climatic influences on tree growth are weaker than would be expected in trees growing at a climatically induced treeline where temperature is the limiting factor [29]. At the same time, the Mt. Etna trees are growing at an elevation that is too high to be strongly affected by summer drought as in Mediterranean lowlands [19]. The intermediate elevation between the two extremes (high elevation where temperature is limiting and low elevation where summer drought is limiting) makes it difficult to explain the tree-growth variability using meteorological data. The low sensitivity of tree growth to climate suggests that neither i) an increase of surrounding air temperature caused by heating from magma at shallow depths, nor ii) an increase in water availability induced by pre-eruptive subsurface pressures and water vapour, is likely to have enhanced photosynthesis before the 2002/2003 flank eruption. Thus to explain the NDVI signal previously observed [11], one must search for factors (volcanic or not) other than additional water or heat induced by volcanic activity.

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Sadly, Sebastiano Cullotta passed away before the submission of the final version of this manuscript. Ruedi Seiler accepts responsibility for the integrity and validity of the data collected and analyzed. We celebrate the memory of our colleague and friend who tragically passed away while this paper was in preparation.

Author Contributions

Conceptualization: RS JWK PJK RT NH DA SC ME RD PC.

Data curation: RS JWK PJK.

Formal analysis: RS JWK PJK PC.

Funding acquisition: NH ME PC.

Investigation: RS JWK PJK RT DA ME PC.

Methodology: RS JWK PJK RT NH DA SC RD PC.

Project administration: RS RT SC PC.

Resources: JWK PJK RT SC ME RD PC.

Software: RS JWK PJK.

Supervision: ME PC.

Validation: RS JWK PJK NH SC ME PC.

Visualization: RS JWK PC NH.

Writing – original draft: RS JWK PJK RT DA SC ME RD PC.

Writing – review & editing: RS JWK PJK RT NH DA SC ME RD PC.

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Tree-ring width reveals the preparation of the 1974 Mt. Etna eruption

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Ruedi Seiler[1,2], Nicolas Houlié[3,4] & Paolo Cherubini[1]

Reduced near-infrared reflectance observed in September 1973 in Skylab images of the western flank of Mt. Etna has been interpreted as an eruption precursor of the January 1974 eruption. Until now, it has been unclear when this signal started, whether it was sustained and which process(es) could have caused it. By analyzing tree-ring width time-series, we show that the reduced near-infrared precursory signal cannot be linked to a reduction in annual tree growth in the area. However, comparing the tree-ring width time-series with both remote sensing observations and volcano-seismic activity enables us to discuss the starting date of the pre-eruptive period of the 1974 eruption.

Early detection of precursors to volcanic eruptions is important in reducing risks for populations and damage to infrastructures[1–8]. Once a volcanic eruption has started, thanks to modern techniques, we are now able to describe both seismic activity[1–8] and surface deformation[9–12] to constrain the origin of magma through gas changes[13–15] and to understand how magma intrusions propagate[16,17]. Still, we know too little about how the magma moves under the surface during pre-eruptive periods (months to days before the magma reaches the surface). For instance, it is sometimes unclear if magma input from depths is steady[18], or, for how long magma could be stored at shallow depths (and eventually degassed) without being detected by seismic and geodetic networks. If not recorded because of their unconventional or too tenuous appearance, precursors of volcanic activity are lost forever.

Following the studies dedicated to vegetation monitoring from space, we propose to use trees to monitor volcanic activity. Trees are likely not reacting directly to volcanic activity but as it has been proposed they may respond to associated environmental changes[19–22] such as water table variation, gas emissions, atmospheric water vapor or sudden temperature changes. As tree growth largely depends on environmental conditions (i.e., on the local availability of water and nutrients, and temperature during the vegetation season) tree rings have been widely used in the environmental sciences as proxies to assess both local and regional past climate variations[23–25] or photosynthesis rates[26]. As trees form one growth ring each year, tree-ring chronologies may be used as annually resolved, long-term records of past eruptive events. Recently, it has been shown that pre-eruptive volcanic activity occurring during the vegetation period can influence the photosynthesis of trees, as shown by Normalized Difference in Vegetation Index (NDVI) derived from satellite imagery months before the beginning of the 2002–2003 eruption of Mt. Etna and the 2002 eruption of Mt. Niyragongo[20]. These observations were not the first satellite observables of this kind. Before the time of modern remote sensing sensors, a reduced near-infrared (NIR) signal was detected in September 1973 in the area of Monte de Fiore (Fig. 1) prior to the 1974 Mt. Etna eruption[27]. In this case, the start and duration of the NIR signal could not be determined nor was the cause of the signal identified as the eruptive activity started months later. In order to test whether trees were impacted by volcanic activity and with the aim of better understanding the dynamics of the early stages of the 1974 eruptive event, we built ring-width time-series of trees located near Monte de Fiore.

The 1974 eruption is key in the recent eruptive history of Mt. Etna when investigating how the magma feeding systems works. The eruption of January–March 1974 represents a petrological transition between two eruptive periods during which different types of magma were emitted: a phenocryst-charged basalt type, which was observed coming from the central vent until 1974, and a more glassy basalt type, free of plagioclase that has been observed in many occasions since 1974[28,29] and at least until the 2001–2003 flank eruption[30]. According to

[1]Swiss Federal Institute for Forest, Snow and Landscape Research WSL, Zürcherstrasse 111, 8903 Birmensdorf, Switzerland. [2]Department of Geography, University of Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland. [3]SEG - IFG, Eidgenössische Technische Hochschule (ETH), 8093 Zürich, Switzerland. [4]MPG – IGP, Eidgenössische Technische Hochschule (ETH), 8093 Zürich, Switzerland. Correspondence and requests for materials should be addressed to R.S. (email: ruedi.seiler@wsl.ch)

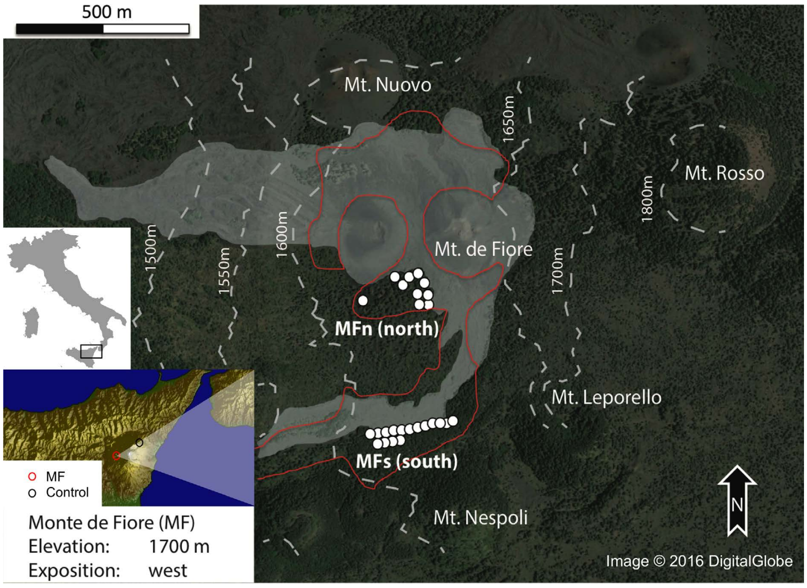

Figure 1. Monte de Fiore sample locations. Local aerial view of Monte de Fiore on the western flank of Mt. Etna near the 1974 vent. Location of trees sampled are marked with white dots, the area of the NIR signal[27] with a red line, and the 1974 lava flow with grey shading. The map of Italy was created using the program R (Version 3.1.3; URL: http://www.R-project.org/)[60] and the topographic map showing Sicily was created using Generic Mapping Tools (Version 5.2.1; URL: http://gmt.soest.hawaii.edu/)[61]. The main map showing the Monte de Fiore area was derived from Google earth (Google, DigitalGlobe, 2016)[62] supplemented with contour lines[63] displaying topography.

Rittman's classification[31], the 1974 eruption was either eccentric[32], eccentric with deep origin[30,33] or lateral[30,34]. Because of the lack of phenocrystals in the emitted basalts[33], it has been proposed that the magma quickly ascended[33] from a source located 11 km below ground[30], corresponding to the depth at which the Mt. Etna magma chamber has been constrained[12,35,36].

The 1974 eruption (30 January 1974–March 1974) was preceded (~10 days) and accompanied by one of the greatest seismic crisis ever observed on Mt. Etna[34,37] with up to 150 events per day detected at the Mt. Vetore station (20 events per day at the Catania station; Fig. 2 and Material and Methods section). For reference, during the 1971 crisis, the daily seismic rate did not exceed 10 events per day at the Catania station[38]. The occurrence of seismic crisis before an eruptive period is not surprising. It is well known that seismic activity precedes volcanic activity[39–43], also on Mt. Etna[3,37,40,44–47] and afterwards is often associated with magma intrusions. Before the onset of the January 1974 eruption, Mt. Etna was already seismically active. In the summer-autumn 1973, a seismic event triggered the deployment of a seismic network on Mt. Etna[48]. Unfortunately, due to technical issues, the locations of the October events, could not be determined with certainty. The temporal coincidence of the October 1973 seismic crisis with both renewed activity at the Voragine and the NIR signal, raises the question of the presence of an early intrusion into the western flank in the vicinity of Monte de Fiore.

In this study, we (i) evaluate whether the ring-width time series of Monte de Fiore trees changed before and after the eruption, (ii) assess whether the NIR signal detected[27] can be associated with tree-ring growth changes, and (iii) discuss our findings in the context of geophysical observations made between September 1973 and March 1974.

Results

We sampled two groups of trees: MFs, south of the southernmost 1974 lava flow, and MFn, in the north close to the Monte de Fiore craters (1737 m a.s.l.). All trees were growing in the area where the NIR signal disturbance was observed[27] (see the red contour line in Fig. 1). In total, we collected 52 cores from 26 trees (*Pinus nigra* J. F. Arnold) growing in the area close to the 1974 eruption at Monte de Fiore (MF). MFn trees are located very close to the 1974 eruptive craters and include 10 trees, whereas the 16 trees of MFs are farther away along the lava flow that originated from Monte de Fiore (Fig. 1). Since the trees were located close (<1 km) to the Monte de Fiore craters, their growth was probably disturbed by projectiles, lava-flow heat[49] and fires during the 1974 eruption. We expected MFn trees to be more disturbed than the MFs trees as they were closer to the 1974 vents. In order to establish the growth of an undisturbed control group, we sampled the cores of 50 control trees of the same species, located on the north-eastern flank of Mt. Etna 13 km away close to Piano Provenzana (control group) at an elevation of approximately 1700 m a.s.l. The growth of these trees was probably not disturbed by volcanic activity during the 1970s and 1980s because there was little eruptive activity during this period along the North-East rift.

Tree-ring growth. Most of the trees in MFn germinated in the 1950s and are younger than trees in MFs, which mostly germinated between 1910–1920 (Supplementary Fig. S1). The similar tree ages in each of the two groups suggest that the germination of the trees probably happened after disturbances such as wildfire or clear cutting.

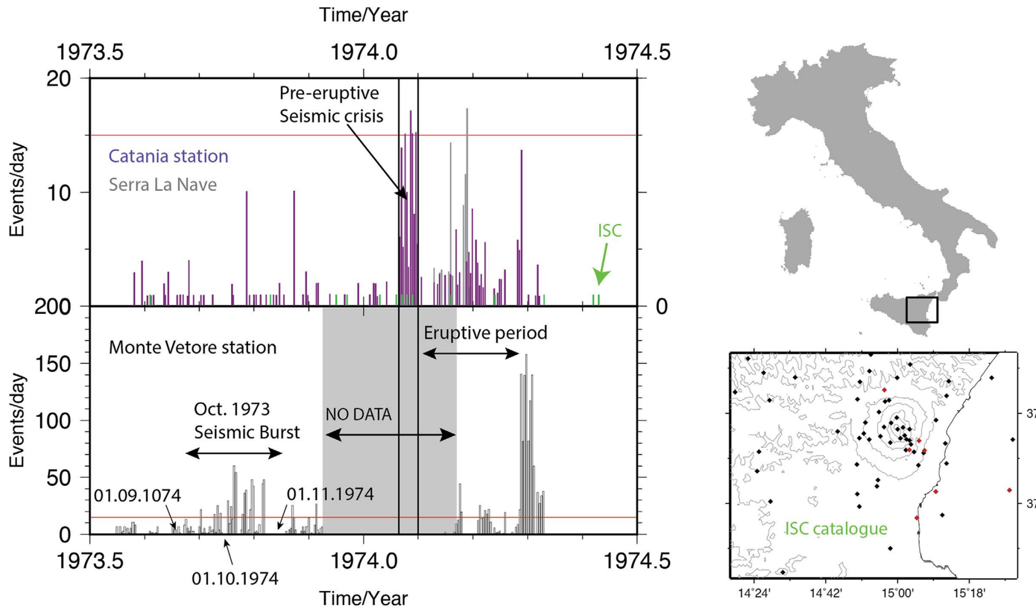

Figure 2. Seismic activity. Seismic activity as detected by seismic sensors deployed on the flanks of Mt. Etna and its surroundings between the summer 1973 and the summer 1974. International Seismological Center (ISC) data is shown with green bars, daily rates of seismicity measured at different stations are grey and purple[37,44]. The black dots are events between January 1970 and January 1980 and the red dots are events between 1973.6 and 1974.6 from ISC.

Nine out of ten trees in MFn did not form any rings during two consecutive vegetation seasons (1974 and 1975; Fig. 3a), probably because of the heat radiating from the lava. Trees at other sites on Mt. Etna have also been found to lack tree rings close to lava flows[49], and we explain these observations as only one hour of exposure to temperatures of 60 °C is able to decrease tree growth[50]. In contrast, trees in MFs located close to a lava flow but far away from the crater formed regular rings during 1974 and 1975 and seemingly were not affected by the heat emitted by the lava flow (Fig. 3b). Before comparing the tree-ring width of 1973 with the ring width of previous years, we need to correct for the age-related growth trend in trees. Only then will it be possible to discuss whether the observed reduction of photosynthesis was already sustained before September 1973.

Age-growth relationship. Tree growth varies over the lifespan of a tree. Such ontogenetic variation strongly impacts the shape of the raw tree-ring width time-series, an effect also known as "age trend"[51]. For dendrochronological purposes, age trends are removed using standardizing methods depending on what growth information is needed[52]. In this study, we used a 30-year spline detrending where a "moving window" is used to standardize the raw data series[51] together with a variance stabilization to obtain equally balanced chronologies which preserved the short-term variability[52,53]. In Fig. 4 the detrended ring-width data for trees in MFn (a), MFs (b), both parts of Monte de Fiore (c) and the control site (d) are shown. After detrending the low-frequency variability of the raw time series is eliminated but high-frequency variability, such as the reduced growth of MFn trees during 1974–1975, is preserved.

Tree-ring patterns are affected by changes in the forest stand structure that changes competition processes for resources such as water and light[54,55]. The tree-ring width patterns of the sampled trees might be affected by changes in the stand during the past decades, e.g., those induced by the death of trees. However, the ring-width patterns of our samples do not show any evidence of changes in competition, e.g., abrupt growth changes except for the growth release of MFn trees during the time after the 1974 eruption, most likely effects of reduced competition caused by burning of some trees After correction for the age trend, the erratic growth of MFn trees and the slow decrease in the growth of MFs trees after 1974 in the raw ring-width data are no longer visible (Fig. 4). Comparing the ring widths of 1973 and 1974–1975 with those of the preceding years 1968–1972 (Fig. 5) suggests that none of the trees showed disturbed growth during 1973, but the growth was strongly reduced or completely suppressed in MFn in 1974 and 1975. Thus, tree growth in this area was significantly impacted only after the eruption (t-test; $p < 0.01$).

Response to climate. The internal correlation coefficient (inter-correlation) for the Monte de Fiore series is 0.6 (Table 1), which suggests that all trees were growing synchronously. Furthermore, the patterns in tree growth in Monte de Fiore (MF) and Piano Provenzana (control; north-eastern rift zone; inter-correlation = 0.53) were similar. Over the last 100 years from 1915 to 2014, the correlation between MF and control age-detrended ring width was 0.5 ($p < 0.001$, Supplementary Fig. S2) despite the sites having different expositions and being approximately 13 km apart. This inter-group correlation suggests that tree growth in MF and at the control site during

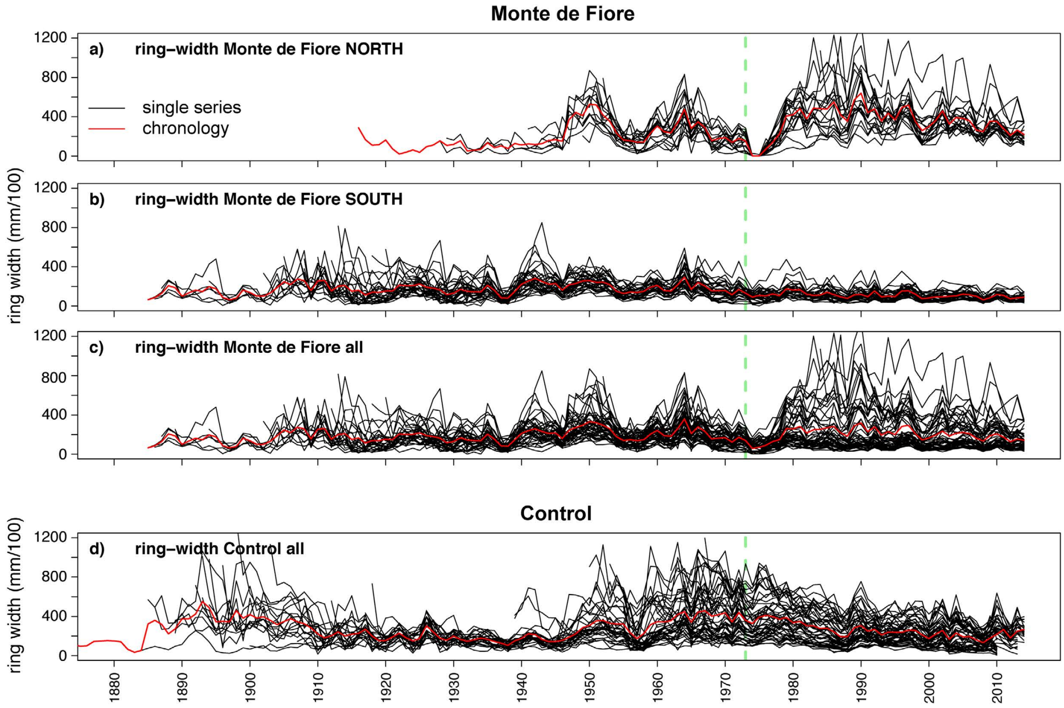

Figure 3. Raw tree-ring chronologies. Ring-width chronologies for trees in MFn (**a**), MFs (**b**), both parts of Monte de Fiore (**c**) and the control site (**d**). The vertical green line indicates the time of the eruption. For most MFn trees, which were closest to the vent, growth stopped for two consecutive years following the 1974 eruption. Such an impact is not visible in the tree-ring width time-series of MFs trees. A zoom image for the eruptive period of this figure is available in the Supplementary Materials (Supplementary Fig. S4).

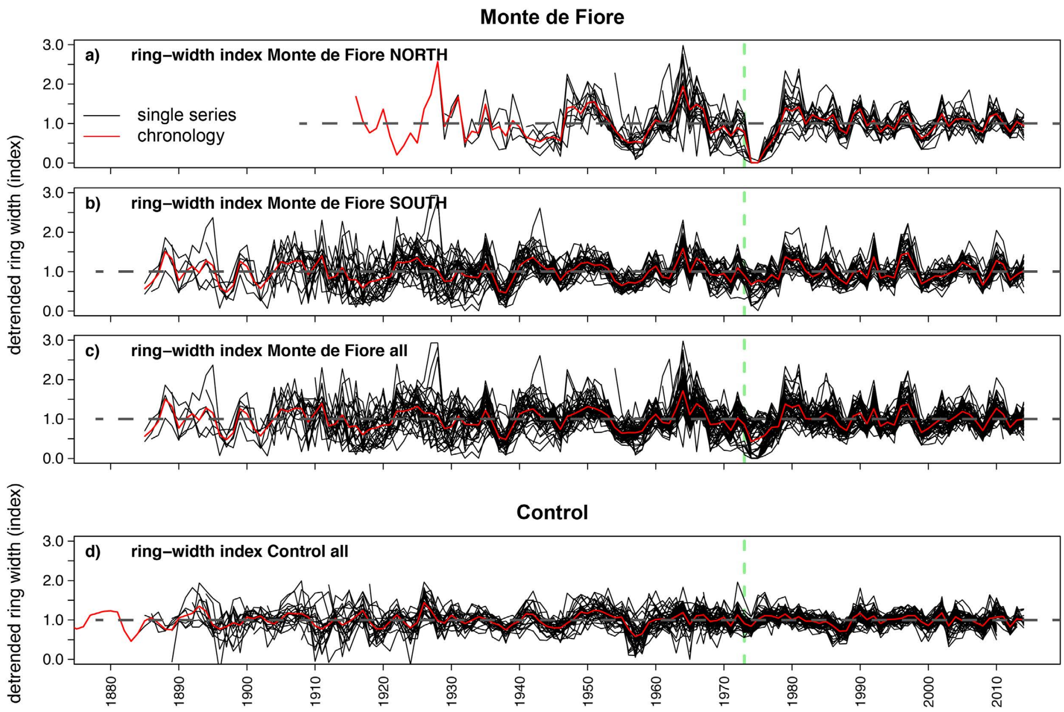

Figure 4. Detrended tree-ring chronologies. Same data as in Fig. 3 after applying detrending to samples from MFn (**a**), MFs (**b**), all of Monte de Fiore (**c**) and the control site (**d**). After correction for the age trend, the growth increase of the MFn trees after 1976 is no longer visible. The vertical green line indicates the time of the eruption.

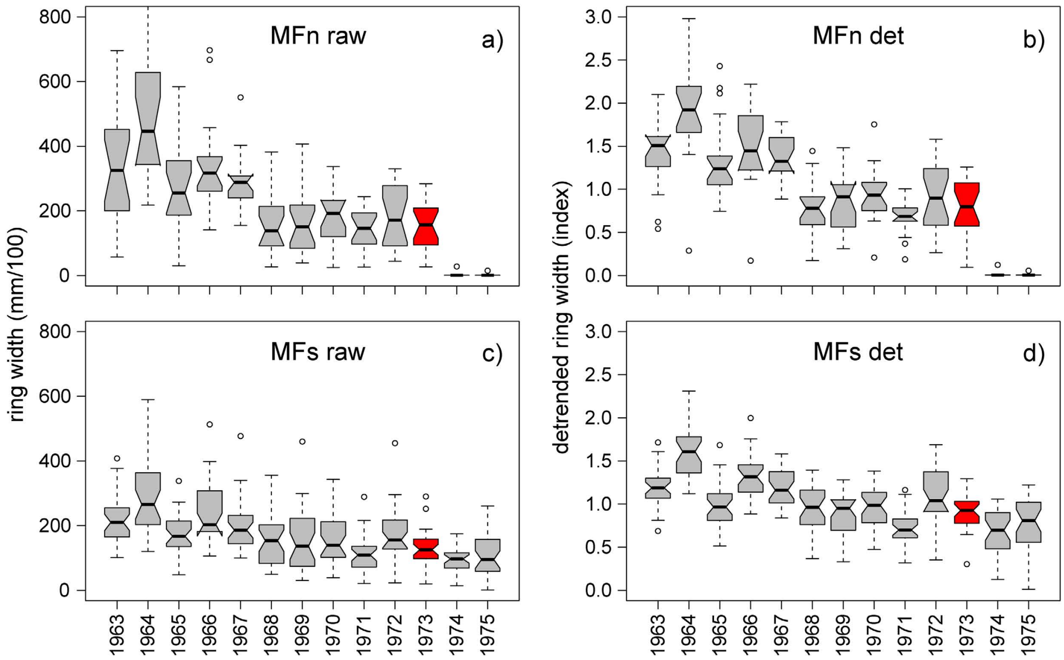

Figure 5. Ring-width comparison. Boxplots showing the median, lower and upper quartiles and the minimum and maximum tree-ring widths of Monte de Fiore samples (raw data [**a**,**c**] and detrended data [**b**,**d**]) in both MFn and MFs. The ring width in MFn and MFs of 1973 is highlighted in red and does not statistically differ (t-test; $p > 0.05$) from the ring width between 1968 to 1972. This indicates that tree growth there was not reduced before the eruption. The ring width of MFn samples was strongly influenced in 1974 and 1975. The reductions in width of both MFn and MFs samples were statistically significant in 1974 and at MFn in 1975 too (t-test; $p < 0.001$).

site	no. of trees	no. of cores	length (yr)	ser. interc.	mean length (yr)	elevation (m a.s.l.)	species
Control	**50**	**76**	**195**	**0.529**	**82.7**	~1600	*Pinus nigra*
Monte de Fiore	**26**	**52**	**130**	**0.597**	**95**	~1700	*Pinus nigra*
MFn	*10*	*20*	*99*	*0.660*	*72.3*		
MFs	*16*	*32*	*130*	*0.614*	*109.3*		

Table 1. Sample overview information. Description of each dataset (Control and Monte de Fiore south, MFs, and north, MFn) in study, with number of trees and cores, total length of group chronologies, series intercorrelation (ser. interc. = measure of common growth signal in the chronology), mean sample length, elevation and species.

this period (Supplementary Fig. S2) was mostly influenced by common factors (i.e. weather, climate, nutrient availability, volcanic activity).

To quantify the impact of climate variations on tree growth, we used interpolated temperature and precipitation anomalies (1924–2004) from the CRU databank (Climatic Research Unit, University of East Anglia, Norwich, U.K.)[56,57] and compared them to tree-growth patterns. Tree-growth at similar elevations on Mt. Etna was shown to be weakly influenced by climate variability[58]. We found that only variations in July precipitation significantly affected trees in MF ($r < 0.23$; $p < 0.05$). This effect, however, was weak. Climate had a stronger influence on the control chronology (Supplementary Fig. S3), with positive precipitation-ring width correlations during summer ($0.22 < r < 0.35$; $p < 0.05$), and temperature-ring width correlations in August ($r = -0.4$; $p < 0.001$) and March ($r < 0.35$; $p < 0.01$). The rather low correlations are supported by observations in Mediterranean area at similar elevations[59]. Temperature and precipitation thus do not seem to strongly affect tree growth at Monte de Fiore. No eruption precursory signals could be found in the tree-growth time-series (Fig. 5c and d). This suggests that the NIR signal observed from SKYLAB was either i) not sustained before September 1973 and therefore had no impact on tree growth, or ii) was sustained but occurred after the vegetation period.

Response to volcanic activity. Consequences of pre-eruptive volcanic activity on tree growth strongly vary with the nature of the processes in place. Volcanic activity has been associated with enhanced photosynthesis during pre-eruptive periods[27]. In other contexts, as in the Mammoth mountains in 1990s[60] and possibly also in Pico del Nambroque, La Palma in 1949[61], pre-eruptive volcanic activity led to tree damage or even die-off. Similarly, the observed decrease in NIR reflectance on the western flank of Mt. Etna[27] may have been caused by processes

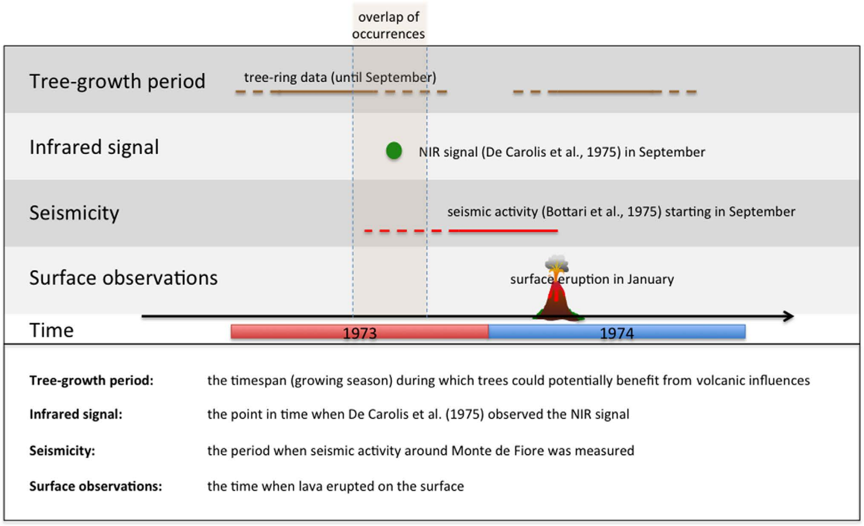

Figure 6. Activity observations in time. Timeline of observations available (tree growth, NIR, seismicity and surface observations) before and after the 1974 eruption activity. Because tree rings are formed until the end of August, the NIR-signal was probably not sustained during the growth season of the Monte de Fiore trees. Seismicity started in September 1973, which coincides well with the time of NIR measurement. The figure was created using Adobe Illustrator[64].

associated with the inception of the 1974 event. In September 1973 at the time of the SKYLAB observation[62], the NDVI processing technique had not yet been developed[63]. Because only the NIR band was available, it is challenging to identify the nature of the process responsible for the detected signal. If the NDVI method had been used with both red and infrared bands, it would have been possible to distinguish between changes of vegetation canopy reflectance and ground temperature.

Growth analyses on trees growing at latitudes comparable to Mt. Etna have shown that tree growth stops after August even though photosynthesis may still be active[64]. Then, if precursory activity had changed the ecological settings around the trees during the growth period of 1973 (March–August 1973), associated signals would be visible in the ring-width time-series. The reduced NIR signal observed with SKYLAB in 1973 may have been caused by higher soil moisture[65,66] due to degassing of large amounts of volatiles[67,68] or a decrease in the photosynthetic activity in the area[27,69,70]. The 1973 ring widths do not differ statistically (t-test; $p > 0.1$) from those of the previous five years (1968–1972) as discussed earlier. If a change in volcanic activity affected tree growth in the area, it must have started at the end of, or after, August 1973. However, the end of the detected NIR signal cannot be constrained in time using tree-ring width analysis as trees are not reacting to environmental influences after the end of the growth season. Here seismic activity might help, as the seismic event of 1973 lasted until the end of October. This date might then be the end of the magma intrusion. At last, in the light of observations collected/comprised in this study, we suggest that the SKYLAB NIR anomalous signal may have been the result of an early dyke intrusion, initializing the 1974 eruptive event. Observed seismic[34,37] and explosive (at central crater) activity during the months of September and October 1973[34] (see Material and Methods section) further support this hypothesis and may help dating the end of the intrusive episode.

Conclusion

In September 1973, a reduced NIR reflectivity was detected on the western flank of Mt. Etna[27] at a location where four months later the 1974 eruption occurred. Seismicity, renewed activity at the central vent[37,48] and remote sensing historical datasets suggest that magma was intruded into the western flank of the volcano months before the January 1974 eruption (Fig. 6). The NIR signal may have been caused by the soil moisture due to gas condensation near the surface, which reduced the NIR reflectance. Such a positive change of the ecological settings would have had a positive influence on tree growth if it had been sustained during the growth season. However, the analyses of the ring widths of tree samples collected in the Monte de Fiore area indicate that, if volcanic activity was indeed causing the anomalous NIR signal, the pre-eruptive period of the 1974 event started by the end of August 1973 at the earliest. This would imply that the duration of the pre-eruptive activity was of the order of a couple of months, which is well compatible with lengths of other pre-eruptive periods observed at Mt. Etna: 6 days in July 2011 before the start of the south flank event[5], only weeks in in autumn 1985[71], in 1989[44,46] and in 1998[3], while on some occasions lasting months before the onset of eruptions[3,37,40,44–46]. Our study has shown that tree-growth histories can help dating the occurrence of early magma intrusions, and that analyzing tree rings can provide valuable information on pre-eruptive volcanic processes. We therefore encourage the use of such tree-ring analyses when reconstructing the processes involved in past volcanic events.

Materials and Methods

Tree ring width analysis. Trees were sampled at 1.3 m height using a 0.5 cm diameter corer 40 cm in length. To account for variability in individual tree growth, two cores were taken from opposite sides of each tree (180° from each other). Each core was glued on a wooden support and prepared by sanding the surface with decreasing grain-size sandpaper so that the tree-ring width could be dated and measured accurately.

We used a Leica Wild M32™ binocular microscope (25–50x magnification) connected to a LINTAB measuring device, coupled with a computer running TSAPwin (Time Series Analysis Program) software (RinnTech, Heidelberg, Germany), to measure the ring widths of our samples with a resolution of 0.01 mm. To assess the quality of the single measurements of the two cores extracted from each tree and to assure that no rings were missing, we crossdated the ring-width patterns of each tree sample-pair visually (TSAPwin) and statistically (COFECHA)[72,73]. On average, all series cover a period longer than 70 years (see chronology statistics in Table 1).

Seismicity levels. During the autumn of 1973, the west flank of Mt Etna was the place of an intense seismic activity. The analysis of the daily seismicity rates at the Mt. Vetore seismic station suggest that seismicity in September-October 1973 was either larger than the seismic activity of late January 1974 or the events were located closer to the seismic instrument. We favor the second hypothesis as the Catania station was detecting less activity in October than in January. During this short seismic survey (10.11–15.11.1973), it was determined that 1) the strongest signals were detected in the western quadrants (stations GVD, VTD, and DNZ and 2) the weakest ones were recorded between East and North directions (stations MSL, CVD, MAR and BVC). The source of the October-November period correspond well to the location of the western flank. The spatial analysis made there could not be supported by other permanent stations already installed at the time along the flanks of the volcano. At the start of the 1974 eruptive period, the seismic sensors located at Serra La Nave (37°41′30″N, 14°45′22.9″E)[74] were not functioning since the 5th December 1973[44].

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Author Contributions

R.S. contributed to project planning, fieldwork, laboratory work, data analysis, data representation and writing the manuscript. N.H. contributed to the project idea, project planning, fieldwork, data representation and writing the manuscript. P.C. contributed to the project idea, fieldwork, data analysis and writing the manuscript. All authors reviewed the manuscript.

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Tree-ring stable isotopes and radiocarbon reveal pre- and post effects of volcanic eruptions on trees at Mt. Etna (Italy)

Ruedi Seiler[1], Irka Hajdas[2], Matthias Saurer[3], James W. Kirchner[1,4], Nicolas Houlié[5], Paolo Cherubini[1]

[1]Swiss Federal Institute for Forest, Snow and Landscape Research WSL, Zürcherstrasse 111, 8903 Birmensdorf, Switzerland

[2]Laboratory of Ion Beam Physics, ETH Zürich, Otto-Stern-Weg 5, 8093 Zürich, Switzerland.

[3]Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

[4]Department of Environmental Systems Science, ETH Zurich, Zürich, Switzerland

[5]Department of Earth Sciences, ETH Zurich, Zürich, Switzerland

Abstract

An enhanced Normalized Difference in Vegetation Index (NDVI) signature detected on Mt. Etna (Italy) in 2001 and 2002 was detected along a distinct line, where, in November 2002, a flank eruption occurred. Dendro-climatological analyses on tree cores of black pine growing along this line revealed that climate variability did not cause the NDVI anomaly. These observations suggest that pre-eruptive volcanic activity may have enhanced photosynthesis along the future eruptive fissure.

However, it is unclear to what extent, the increased photosynthesis can be attributed to volcanic activity prior to the subsequent flank eruption.

Here we analyze stable carbon and oxygen isotope ratios and radiocarbon within tree rings to assess the influence of volcanic activity on tree-ring properties before and during the 2002/2003 flank eruption.

Our findings suggest that during the eruption trees took up water with a lower oxygen isotopic ratio compared to normal and that they may have been exposed to pre-eruptive CO_2 degassing, which could have resulted in a fertilizing effect and would be a sensible explanation for the enhanced NDVI signature.

Introduction

Early detection of precursors to volcanic eruptions can help in preventing major damage and loss of life. Ground deformation and changes in seismicity, geochemistry, petrography, and gravimetry are regularly used to assess volcanic activity before eruptions (e.g., McNutt, 1996; Battaglia et al., 1999; Williams-Jones & Rymer, 2002; Sherburn et al., 2007; Hooper et al., 2012; Sicali et al., 2015). Ascending magma in volcanoes can be revealed by surface deformation, micro-seismicity, and the release of volcanic gases (Gerlach, 1991; Farrar et al., 1995; Aubert, 1999; Sparks et al., 2012). Volcanic activity is usually detected by remote sensing techniques, which include the acquisition of geochemical and geophysical parameters recording phenomena related to volcanic activity, such as gas emissions and hydrological variations, over time (e.g., McNutt et al., 2000; Andronico et al., 2009). Studies on Mt. Etna (Italy) using satellite imagery detected pre-eruptive anomalies in near infrared reflectance and in Normalized Difference in Vegetation Index (NDVI), demonstrating that vegetation can also be locally affected by pre-eruptive activity months or years before the onset of eruptions (Romero & Bonelli, 1951; DeCarolis et al., 1975; Houlié et al., 2006). An enhanced vegetation index (NDVI) was detected along a distinct line, which later developed into an eruptive fissure, over two consecutive years before the 2002/2003 flank eruption on Mt. Etna (Houlié et al., 2006).

The processes leading to local changes in pre-eruption tree growth related to volcanic activity are still not understood. A study which analyzed climate - tree growth relationships on Mt. Etna suggested that climatic effects on tree growth are unlikely to have caused the abovementioned NDVI anomaly, implying that it may have arisen from other, as yet unknown, factors related to volcanic activity (Seiler et al., 2017a). Regarding post-eruption effects, it has been shown that photosynthetic rates of trees can be enhanced on a global scale by an increase in diffuse light caused by volcanic aerosols after eruptions (e.g., Gu et al., 2003). On the other hand, many studies have shown growth decreases after major volcanic eruptions (e.g., Büntgen et al., 2005; Krakauer & Randerson, 2003). Tree growth is therefore potentially useful for investigating both pre- and post-effects of volcanic eruptions (e.g., Seiler et al., 2017b). After they are formed, tree rings remain unaltered and are stored within the plant structure (McCarroll & Loader, 2004), providing annually resolved archives that have been widely used to reconstruct past climatic conditions and events (Levin & Kromer, 2004).

Isotopic ratios of the stable carbon isotopes ($\delta^{13}C$) in tree rings reflect a combination of atmospheric composition and tree-physiological responses to environmental changes (Francey & Farquhar, 1982), and are frequently used to study stomatal activity, water use efficiency and the influence of climatic conditions over time (e.g., Duquesnay et al., 1998; Porter et al., 2009). Stable oxygen isotope ratios ($\delta^{18}O$) have been widely used to assess leaf transpiration, climate variability, and also water sources (e.g., precipitation, soil water or groundwater) used by trees (Ehleringer & Dawson, 1992; Lee et al., 2007; Leonelli et al., 2017). The analysis of these isotope ratios can therefore help elucidate causes of past volcanic eruptions. Recently, changes of $\delta^{18}O$ in groundwater preceding earthquakes on Iceland were reported (Skelton et al., 2014), suggesting that seismic activity, such as takes place before and during volcanic eruptions, may be associated with infiltration of magmatic water into groundwater.

In addition to stable isotopes, radioactive isotopes are useful tracers for the uptake of depleted gasses (e.g., fossil carbon dioxide; Saurer et al., 2003; Donders et al., 2013). Radioactive ^{14}C decays with a half-life of 5730±30 years (Godwin, 1962) and fossil CO_2 is consequently ^{14}C-dead. Therefore, radiocarbon measurements on wood samples from tree rings not only enable one to determine the ^{14}C-age of the wood structure, but they further allow one to detect possible uptake of fossil CO_2 by the trees.

Studies of the influence of volcanic eruptions on $\delta^{18}O$ and $\delta^{13}C$ in tree-ring cellulose found that the ejection of large amounts of dust reduced solar radiation and temperatures and consequently led to higher air humidity, thus decreasing $\delta^{18}O$ values (Battipaglia et al., 2007). Further, studies of ^{14}C in tree rings have shown that trees growing near natural CO_2 springs take up fossil CO_2 and their growth increments contain lower levels of ^{14}C (Saurer et al., 2003; Donders et al., 2013). Sulerzhitzky (1971) found that trees growing close to volcanoes also contain lower levels of ^{14}C. Moreover, ^{14}C measurements in tree rings have been used to assess uptake of fossil carbon by trees exposed to elevated concentrations of CO_2 and CO from fossil fuel combustion from vehicular traffic (Battipaglia et al., 2010). Extensive exposure to elevated volcanic CO_2 degassing could even lead to root impairment (Biondi & Fessenden, 1999). Degassing of CO_2 from volcanic vents and its effect on trees have been demonstrated at the Mammoth Mountain in California (Cook et al., 2001), where signals of reduced ^{14}C levels within the tree-ring structure were found, which demonstrated that trees were taking up volcanic CO_2.

Here we analyze isotopic ratios of $\delta^{13}C$ and $\delta^{18}O$, as well as the content of ^{14}C, in tree rings of trees growing near the eruptive fissure along which Houlié et al. (2006) observed an increase in NDVI, to better understand the influence of volcanic activity on tree growth on Mt. Etna. We aim to i) see if there is an influence of the 2002/2003 volcanic activity on isotopic ratios in tree rings and to ii) evaluate whether the uptake of fossil, pre-eruptive volcanic CO_2 (Allard et al., 1991) by the trees could have contributed to the enhanced NDVI.

Materials and Methods

Study area

Mt. Etna, with an elevation of 3330 m a.s.l. in the northeastern part of Sicily, is the highest stratovolcano in central and western Europe. It is close to the Mediterranean Sea, with a strongly maritime climate on the eastern side (Poli Marchese & Grillo, 2004; Branca et al., 2008) and drier conditions on the western side (Burga & Klötzli, 2004). The lower slopes are characterized by settlements and agriculture (predominantly orchards; Poli Marchese & Grillo, 2004), whereas intermediate elevations (1000-1600 m a.s.l.) are covered by European beech (*Fagus sylvatica* L.), and at higher elevations (1600-1900 m a.s.l.) Corsican black pine (*Pinus nigra* J.F. Arnold) is predominant. Few undisturbed forest stands still exist at the highest elevations, mostly on the northern side of the mountain (Poli Marchese & Grillo, 2004). The the highest vegetation belt is further disturbed in its uphill development by frequent lava flows (17 since 1950; Global Volcanism Program, 2013) originating from lateral flank eruptions (Certini et al., 2001; Dazzi, 2007; Egli et al., 2012), or wildfires caused by other volcanic processes, such as degassing and heat radiation through small vents (Allard, 1997; Aubert, 1999). Predominant soil types are Regosols, Andosols and Cambisols with characteristics depending on the age of the lava flows and volcanic deposits on which they developed (Dazzi, 2007; Lulli, 2007; Egli et al., 2008). Natural and anthropogenic processes, i.e., wildfires, lava flows, avalanches and logging, have heavily impacted the forests on the flanks of Mt. Etna over the past millennia.

Sampling

We collected cores from a total of 51 *P. nigra* trees growing in the immediate vicinity to the eruptive fissure of 2002/2003 close to Piano Provenzana, at an elevation of 1700-1800 m a.s.l. on the north-eastern flank of Mt. Etna (*Figure 1*), using a 0.5 cm-diameter corer with a three-threaded auger (Haglof Inc., Sweden).

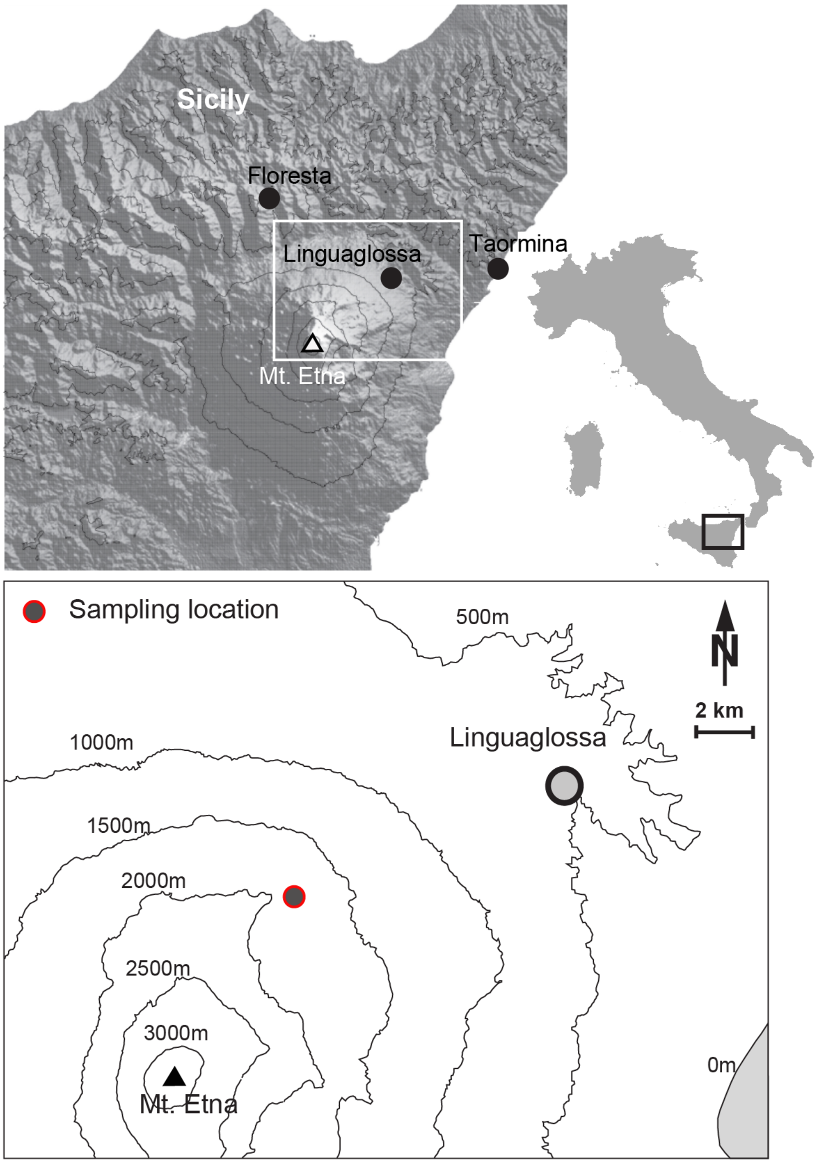

Figure 1 *Sampling location along the 2002/2003 eruptive fissure on the north-eastern flank of Mt. Etna at an elevation range of 1600 to 1850 m a.s.l. The map of Italy was created using the program R (Version 3.1.3; URL: http://www.R-project.org/), the topographic map showing Sicily was created using Generic Mapping Tools (Version 5.2.1; URL: http://gmt.soest.hawaii.edu/) and the base map was taken from Egli et al. (2007).*

Ring-width measurements

We measured ring width to the nearest 0.01 mm using a Leica Wild M32 binocular (Leica, Germany) with 25-50x magnification, coupled to a LINTAB measuring device and a computer running the

TSAPwin (Time Series Analysis Program) software (RinnTech, Heidelberg, Germany). Ring-width measurements were crossdated visually and statistically using TSAPwin and Cofecha (50 year segments with a 25 year overlap) to ensure that no rings were missing and ring-width patterns were in agreement.

Sample preparation

Five tree cores from five different trees were taken to measure stable isotope ratios in the tree rings. Wood samples of tree rings between 1977 and 2006 from five trees were prepared for stable isotope analyses. From four tree cores, wood samples of five consecutive annual rings (1999 - 2003) overlapping the time of eruption, and of an additional five consecutive years (1992 - 1996; i.e., used as control rings formed when no eruption occurred at that location), were selected for radiocarbon measurement.

Single annual rings of selected cores were split and cut into pieces under a binocular with a 25x magnification using a standard laboratory scalpel. After each cutting sequence the material of the split ring was stored in an Eppendorf tube and the workspace and instruments were cleaned using a vacuum cleaner and cleansing tissues impregnated with ethanol/distilled water to prevent mixture of wood fragments over different ring samples.

Stable isotope analyses

We extracted cellulose from wood material using the procedure suggested by Boettger et al. (2007), by applying the following steps. Cut samples of five tree cores were homogenized in an ultra-centrifugal mill at 16'000 rotations per minute. Ten milligrams of the resulting wood powder from each tree-ring sample were enclosed in Teflon filter bags and washed twice with a 5% sodium hydroxide (NaOH) solution for two hours at 60°C. These washing runs remove oils, tannins, fats, hemi-cellulose and resins. To eliminate any remaining lignin we immersed the samples in a 7% solution of sodium chlorite (NaClO2) at 60°C for a total of 30 hours. Samples were then dried in the oven at 60°C overnight.

Following Woodley et al. (2012) and Weigt et al. (2015), we measured ratios of carbon $\delta^{13}C$ and oxygen $\delta^{18}O$ isotopes on CO gas produced by pyrolysis in a TC/EA at 1420 °C, coupled with an isotope-ratio mass spectrometer (delta Plus XP, Thermo, Bremen, Germany), on 1.0-1.2mg of wood cellulose wrapped in a silver cups in a continuous flow of pure He gas. The isotopic ratio of each sample was measured against a reference CO gas, where:

$$\delta\ (‰) = \{(\delta_{sample}/\delta_{standard})-1\} x\ 1000$$

The mass spectrometer was calibrated to international as well as internal laboratory standards and provided a precision of 0.2‰ for $\delta^{13}C$ and 0.3‰ for $\delta^{18}O$.

Due to the release of isotopically light carbon from burning of fossil fuel, atmospheric $\delta^{13}C$ is decreasing with time. Our $\delta^{13}C$ data were corrected for this so-called "Suess-effect" (Keeling, 1979) by adding correction values provided by McCarroll and Loader (2004).

Meteorological data

We calculated the relationship between climate variability and isotopic ratios by using an interpolated monthly temperature and precipitation dataset for the Mt. Etna region taken from the CRU - Climatic Research Unit, University of East Anglia, Norwich, U.K. (e.g., Mitchell et al., 2004).

Mixed effect models

Using a forward-backward approach (Cook & Pederson, 2011) based on the Akaike Information Criterion, we calculated mixed effect models incorporating meteorological variables which explained the greatest variance of stable isotope ratios. To avoid over-fitting, we tested the explanatory variables for collinearity using variance inflation factor analysis (Kurtner et al., 2005). The models were calibrated using the timespan from 1977 to 2006.

Radiocarbon - Preparation methods

After soxhlet treatment, the samples were prepared using two different preparation methods, the cellulose-extraction method (Stuiver & Quay, 1981), and the acid - base - acid (ABA) washing method (Hajdas et al., 2004), to compare differences in ^{14}C content between the two methods. In order to reduce costs and have enough material for both methods and to obtain robust ^{14}C measurements, we made an annual pooling, combining sample material of the same growth year from the four trees selected for radiocarbon measurements.

I. Soxhlet treatment

Earlier studies addressed the importance of standard Soxhlet treatment of organic matter prior to radiocarbon dating to remove ^{14}C contamination (Hajdas et al., 2008). After being placed in a Soxhlet apparatus, samples were immersed in a circulating condensate of hexane, acetone and ethanol for one hour each, following the technique described by Hajdas et al. (2008).

II.a Cellulose extraction

We extracted cellulose from our tree-ring samples by applying a five-step process, during which each sample was immersed in 5ml of 4% sodium hydroxide (NaOH) and hydrogen chloride (HCl) at 75°C alternately for 10h, 1h, 1.5h and 1h respectively. After each step, the samples were rinsed with distilled water until they became pH-neutral (measured with pH test stripes). During the fifth and last step, samples were immersed in 5ml of 5% sodium chlorite ($NaClO_2$) mixed with five drops of 4% HCl at 75°C for two hours before being put into an ultrasonic bath for 15 minutes. At the conclusion of this step, samples were washed neutral in distilled H_2O at 60°C and dried in the oven (Němec et al., 2010).

II.b ABA method

Designed to remove contamination of samples by humic acids and carbonates (De Vries & Bardensen, 1954), the ABA method is the standard chemical pre-treatment of organic matter for radiocarbon dating (Hajdas et al., 2008). Soxhlet-treated samples were first washed in acid solution to remove carbonate contamination from the sample surface. The samples were then washed with distilled water before being immersed into 0.1 M basic sodium hydroxide (NaOH) for one hour to dissolve humic acids. After rinsing to neutral pH, samples were then immersed in an acid bath to remove any carbonates that may have precipitated from modern atmospheric CO_2 dissolved in the NaOH solution.

Graphitisation and ^{14}C measurements

Finally, all samples were washed to pH neutral and dried. An equivalent of 1 mg of carbon was weighed into the tin boats for graphitization using the AGE system (Wacker et al., 2010). AMS analysis was performed on the miniaturized radiocarbon dating system (MICADAS; Synal et al., 2007) at the laboratory of Ion Beam Physics of the ETH Zürich.

^{14}C results calibration

Measurements of fraction ^{14}C ($F^{14}C$ ±1σ) values were used to calibrate the ^{14}C age of our samples using the online OxCal calibration service (Oxford Radiocarbon Accelerator Unit, United Kingdom), applying the calibration setting from 2013 (IntCal13), which includes the bomb-peak information for the Northern Hemisphere (Bomb 13 NH1). Calibrated ^{14}C ages for all samples from both preparation methods (cellulose and ABA) were compared to calendar ages (AD) derived from annual tree-growth rings.

Results

Tree-ring chronologies

The mean raw ring-width chronology is displayed in *Figure 2*. The series intercorrelation of 0.513 (measure of common growth signal in the chronology), as a measure of common growth signal, demonstrates that the tree-ring series of our samples match and crossdate well, allowing the assumption that no tree rings are missing and showing that the calendar ages (AD) of the tree rings are correctly dated allowing to allocate isotopic ratios in wood material of single tree rings to exact calendar age. Tree-ring width chronology statistics and information are shown in *Table 1*.

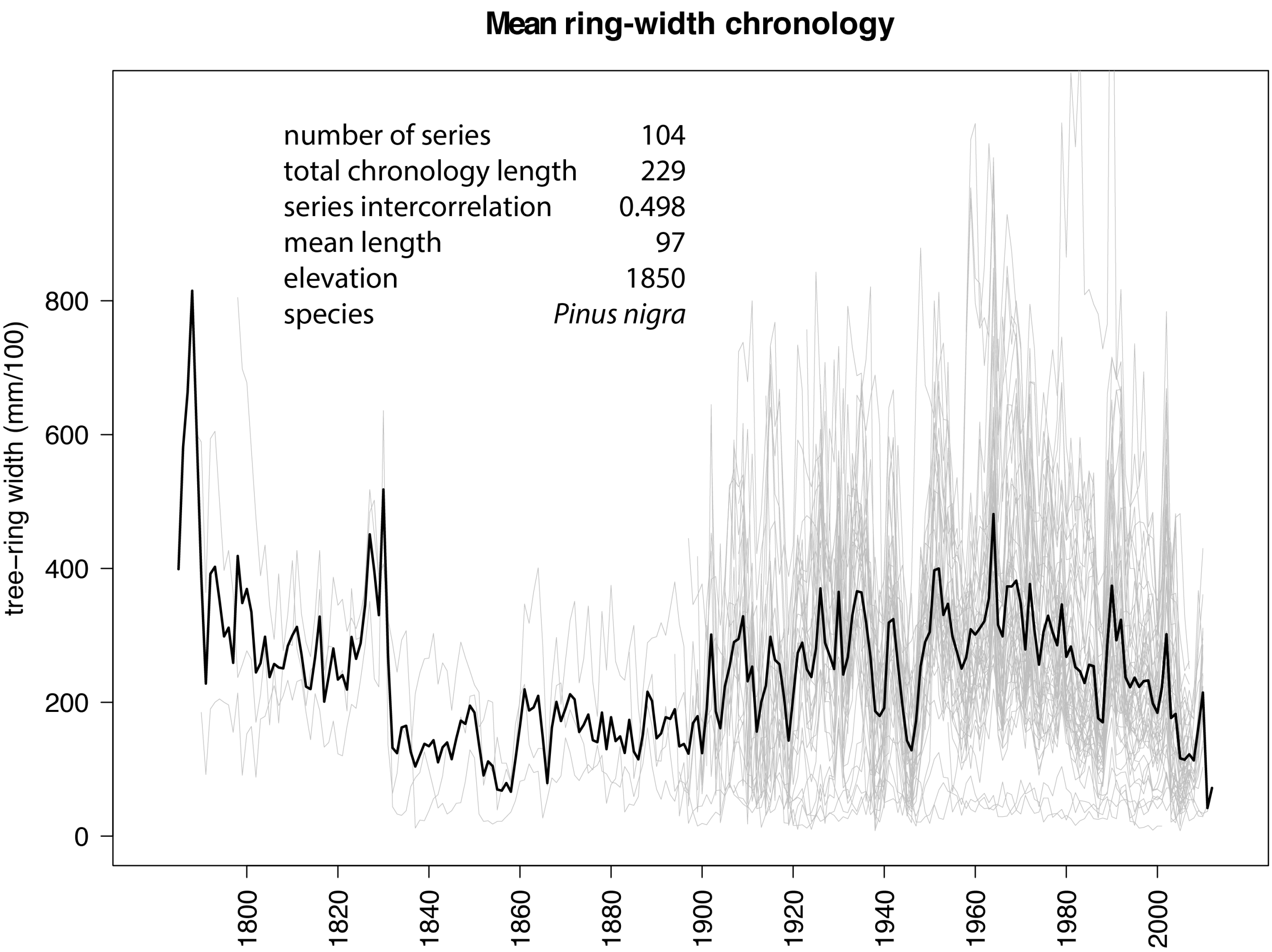

Figure 2 Tree-ring width of single trees (grey) and mean ring-width chronology (black).

Site	no. of trees	total length	ser.interc.	mean length	elevation	species
Piano Provenzana	51	228	0.513	91.7	1850	*Pinus nigra*

Table 1 Descriptive statistics of sample chronology displaying number of trees, total length (years) of the chronology, series intercorrelation (ser.interc. = measure of common growth signal in the chronology), mean sample length (years), elevation (m a.s.l.) and species.

Stable isotopic ratios - $\delta^{13}C$ and $\delta^{18}O$

Tree-ring $\delta^{13}C$ measurements range from -24.70 to -20.33‰, and tree-ring $\delta^{18}O$ measurements range from 30.01 to 34.94‰ (with series inter-correlations of 0.44 and 0.39 respectively). Isotope ratios ($\delta^{13}C$ and $\delta^{18}O$) of single tree cores and stand averages are given in *Table 2*. We performed a running-correlation analysis using an 11-year window to analyze changes in synchronicity between $\delta^{13}C$ and $\delta^{18}O$ ratios over time. The correlations (*Figure 3*) show that, based on the R-values, carbon and oxygen isotope ratio variabilities disagree between 1982 and 1986 ($0<|r|<0.05$; $P>0.9$) whereas from 1989 to 2006 synchronicity is significantly higher ($0.31<|r|<0.78$; $P<0.05$).

year	T1_$\delta^{18}O$	T1_$\delta^{13}C$	T2_$\delta^{18}O$	T2_$\delta^{13}C$	T3_$\delta^{18}O$	T3_$\delta^{13}C$	T4_$\delta^{18}O$	T4_$\delta^{13}C$	T5_$\delta^{18}O$	T5_$\delta^{13}C$	**avg_$\delta^{18}O$**	**avg_$\delta^{13}C$**
1977	33.93	-23.23			32.85	-22.66	33.05	-23.51	33.51	-24.06	33.33	-23.37
1978	33.62	-22.14			33.70	-22.04	32.76	-21.83	32.87	-21.70	33.24	-21.93
1979	34.10	-23.17			33.75	-22.41	33.61	-23.29	33.57	-23.09	33.76	-22.99
1980	33.65	-23.38			32.74	-23.52	33.29	-23.80	33.18	-22.58	33.22	-23.32
1981	34.53	-22.56			32.74	-22.22	34.59	-24.39	33.78	-21.12	33.91	-22.58
1982	34.76	-22.48			33.58	-22.32	34.94	-22.95	34.10	-21.11	34.35	-22.22
1983	33.79	-23.28	33.15	-22.19	33.76	-22.11	33.82	-23.72	33.48	-23.20	33.60	-22.90
1984	33.15	-22.79	32.84	-20.63	34.28	-22.65	33.20	-21.80	32.38	-22.24	33.17	-22.02
1985	33.70	-22.37	33.67	-22.25	33.85	-21.59	34.36	-21.18	33.53	-22.23	33.82	-21.92
1986	33.43	-22.72	32.68	-22.31	34.48	-21.89	32.96	-22.25	32.45	-22.22	33.20	-22.28
1987	32.55	-22.14	32.23	-22.33	33.30	-21.88	32.35	-22.15	31.83	-22.85	32.45	-22.27
1988	32.46	-22.92	31.99	-22.66	32.55	-22.89	33.41	-21.88	32.66	-21.05	32.61	-22.28
1989	32.68	-22.97	33.23	-23.18	32.77	-22.31	32.87	-23.77	32.43	-21.51	32.80	-22.75
1990	32.98	-21.98	32.93	-22.10	32.86	-22.31	33.64	-21.41	33.08	-21.77	33.10	-21.91
1991	33.08	-22.65	32.57	-22.22	33.77	-21.90	33.43	-22.59	32.62	-21.42	33.09	-22.16
1992	33.30	-22.69	32.71	-22.29	32.99	-22.50	32.74	-22.05	32.22	-22.36	32.79	-22.38
1993	32.99	-21.32	32.34	-21.96	32.66	-22.44	33.53	-21.64	32.94	-23.34	32.89	-22.14
1994	32.21	-22.96	32.43	-21.69	32.63	-20.33	33.91	-24.07	32.69	-22.67	32.77	-22.34
1995	31.83	-23.26	31.95	-23.35	34.04	-21.88	33.29	-23.51	32.56	-23.55	32.73	-23.11
1996	32.05	-23.44	32.81	-23.52	33.04	-22.52	33.22	-24.43	32.18	-23.02	32.66	-23.39
1997	33.16	-22.66	33.14	-22.85	32.11	-22.70	33.29	-22.65	31.70	-23.97	32.68	-22.97
1998	32.50	-22.97	33.95	-22.56	33.65	-21.48	34.03	-23.15	32.08	-21.13	33.24	-22.26
1999	32.66	-23.56	32.77	-22.14	32.39	-22.18	33.18	-22.22	31.33	-22.52	32.47	-22.52

2000	31.43	-22.86	32.68	-22.50	32.86	-22.48	33.08	-22.62	31.73	-22.09	32.35	-22.51
2001	33.18	-22.40	33.93	-21.68	33.80	-22.81	33.83	-22.21	33.25	-23.35	33.60	-22.49
2002	32.41	-23.63	33.21	-22.90	32.52	-23.07	33.66	-23.49	32.43	-23.55	32.85	-23.33
2003	30.24	-23.11	31.48	-22.58	30.75	-23.82	30.88	-23.58	30.01	-24.70	30.67	-23.56
2004	31.77	-23.69	34.08	-21.55	33.56	-23.90	32.93	-23.45	31.06	-23.41	32.68	-23.20
2005	30.54	-24.06	32.06	-23.06	33.12	-22.90	32.02	-23.19			31.93	-23.30
2006			33.60	-23.151	32.71	-23.47	33.12	-23.79	32.36	-23.78	32.95	-23.55

Table 2 *Stable isotope ratios (given in ‰) of $\delta^{18}O$ (30.01 to 34.94) and $\delta^{13}C$ (-24.70 to -20.33) of single trees (T1 - T5) and average ratios ($\delta^{18}O$: 30.67 to 34.34 ± 0.67sd; $\delta^{13}C$: -23.56 to -21.91 ± 0.53sd). For years with missing values there was not enough cellulose material to measure isotopic ratios.*

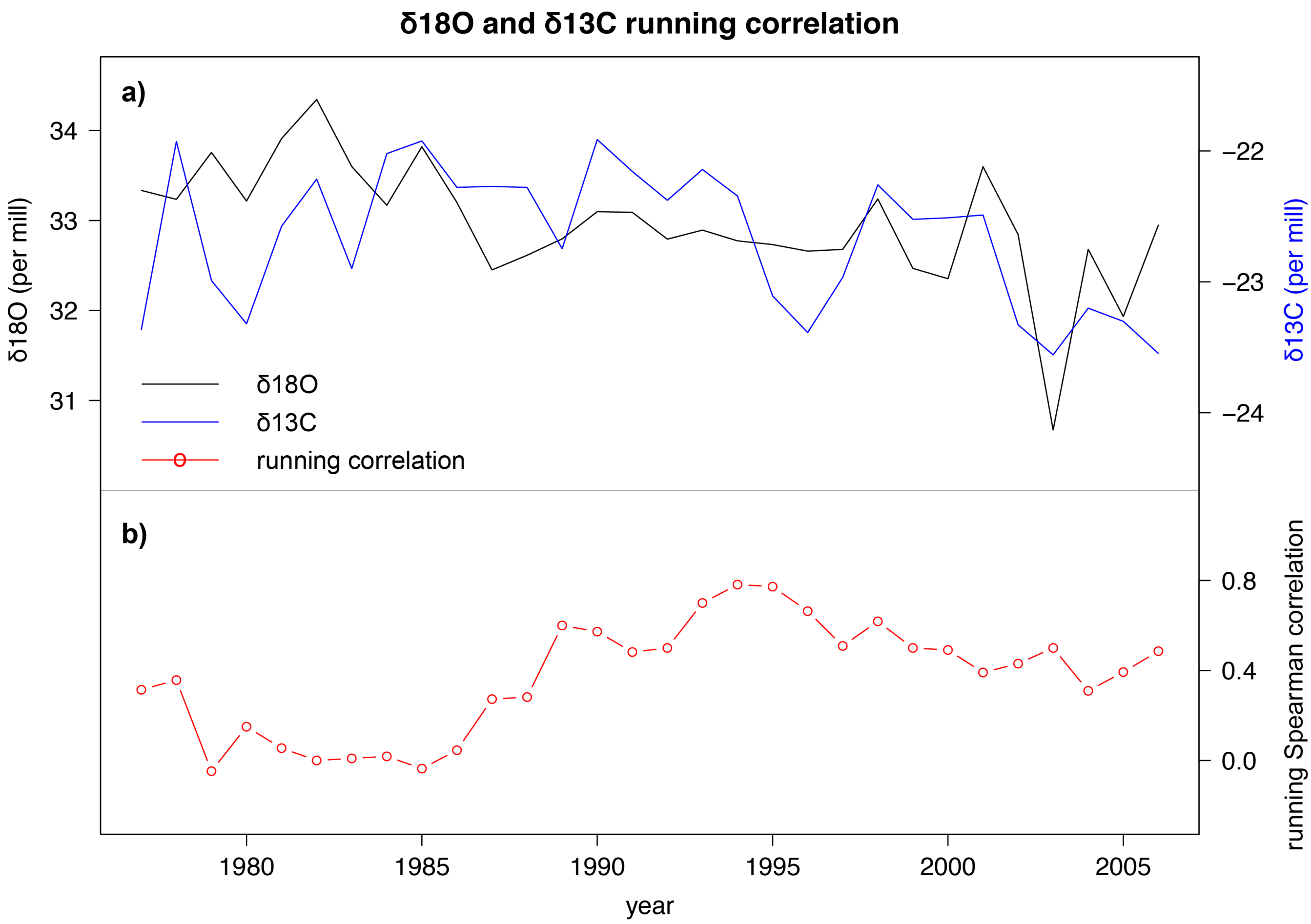

Figure 3 *Average $\delta^{13}C$ and $\delta^{18}O$ chronologies (a) and Spearman rank running correlation R-values from 1977 to 2006 between the two isotopes (b) show an increase in correlation after 1989.*

We applied a linear detrending to our stable isotope data to remove any long term positive or negative trend and to distinguish between correlations influenced by high- and low-frequency variability in the data (Cook & Kariukstis, 1990).

Based on Spearman rank correlations (*Figure 4*) for the pre-eruption period 1977-2002, the raw and detrended tree ring $\delta^{13}C$ values are positively correlated with temperatures in September (r = 0.441 and 0.412; $P < 0.05$) and October (r = 0.403 and 0.418; $P < 0.05$). Further, the raw $\delta^{13}C$ measurements are negatively correlated with precipitation in June (-0.393; $P < 0.05$) and the detrended $\delta^{13}C$ measurements are negatively correlated with precipitation in August (-0.434; $P < 0.05$). Both raw and detrended $\delta^{13}C$ measurements revealed a common response to climate parameters, indicating that the response is caused by short-term variability.

Moreover, the raw tree ring $\delta^{18}O$ is negatively correlated with temperature in August (r = -0.41; $P<0.05$), in contrast to the detrended tree ring $\delta^{18}O$, which is positively correlated with temperature in June (r = 0.565; $P<0.05$) and negatively correlated with precipitation in June (r = -0.42; $P<0.05$).

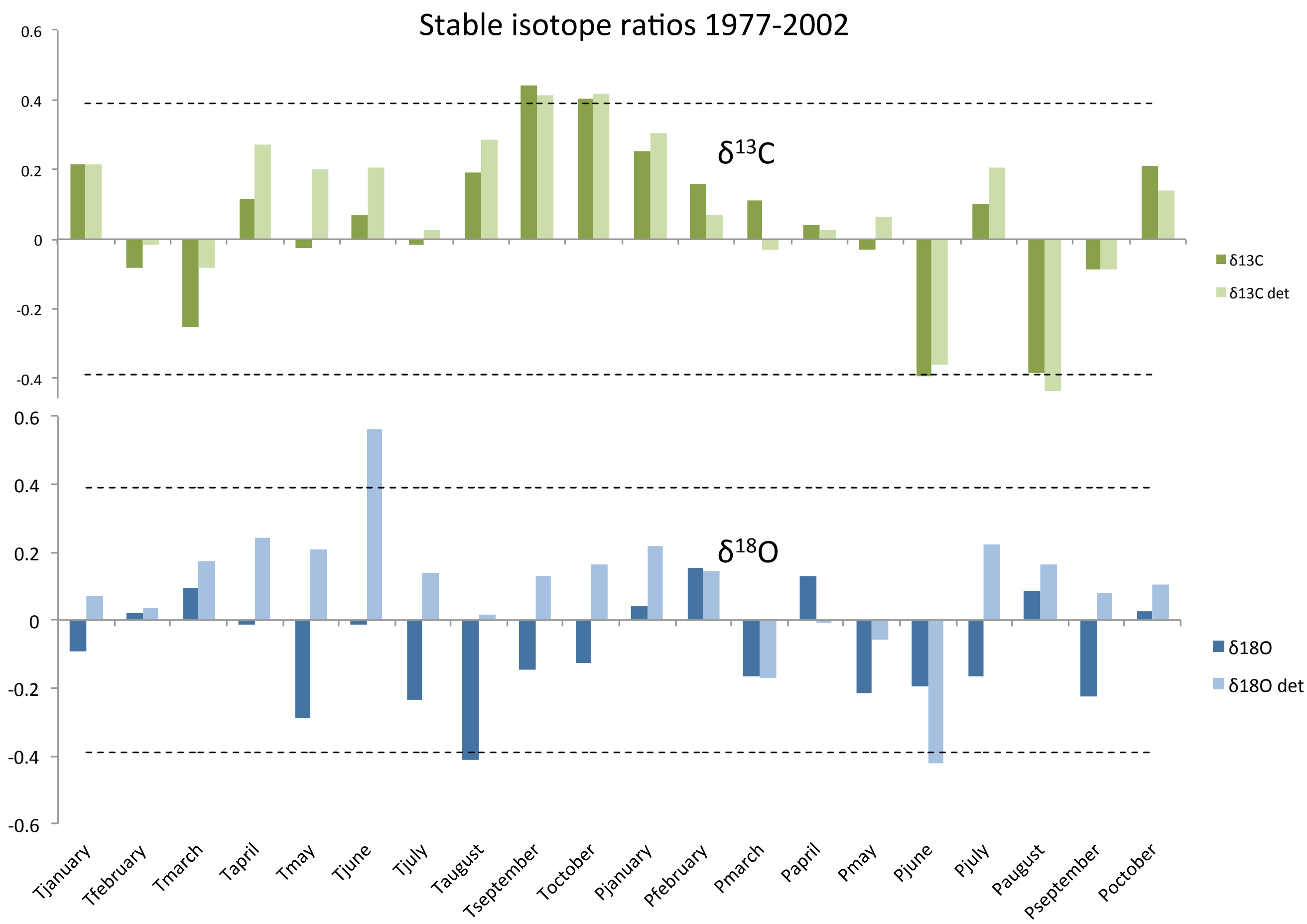

Figure 4 *Spearman rank correlations between stable isotope ratios and climate variables, where T=temperature and P=precipitation. The 95% significance levels are indicated by interrupted lines.*

Therefore, the contrasting correlations between raw and detrended $\delta^{18}O$ stable isotope ratios with climate variables are obviously caused by a long-term trend. The long-term decreasing trend in the oxygen stable isotope ratios is inversely correlated with a generally increasing trend in summer temperatures, leading to the negative correlation with temperature in August. Based on the variables significantly correlating with short-term variations of $\delta^{18}O$ (i.e., temperature and precipitation in June) the strongly reduced $\delta^{18}O$ in 2003 cannot be explained by any of these two variables, which do not significantly deviate (t-test; $P > 0.05$) for that particular year.

Further, the mixed-effect model explains 50 % (adjusted R^2; P < 0.001) of $\delta^{13}C$ variability, demonstrating that the ratio of heavy to light stable carbon isotopes is predominantly influenced by climate, also before and during the eruption of 2002/2003 (*Figure 5-1*).

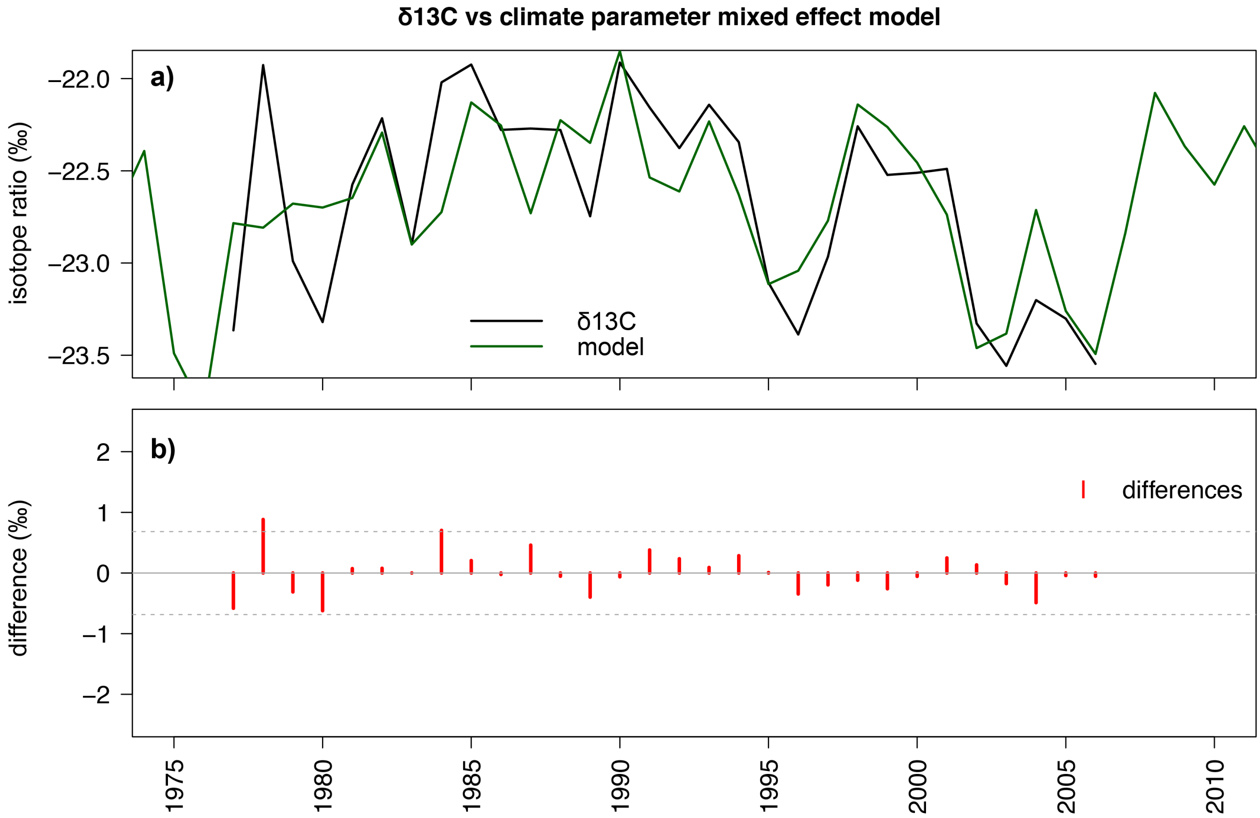

Figure 5-1 Raw $\delta^{13}C$ variability and the mixed effect models are shown in the top panel (a). The deviation between measurements and models (measurements - model) is shown in the bottom panels (b).

In contrast, the mixt-effect model explains 24% (adjusted R^2; $P < 0.05$) of $\delta^{18}O$ variability between 1977 and 2006; moreover, the strong reduction in 2003 exceeds the two-standard-deviation limit and is not explained by the model, suggesting that climate is unlikely to have caused this reduction (*Figure 5-2*).

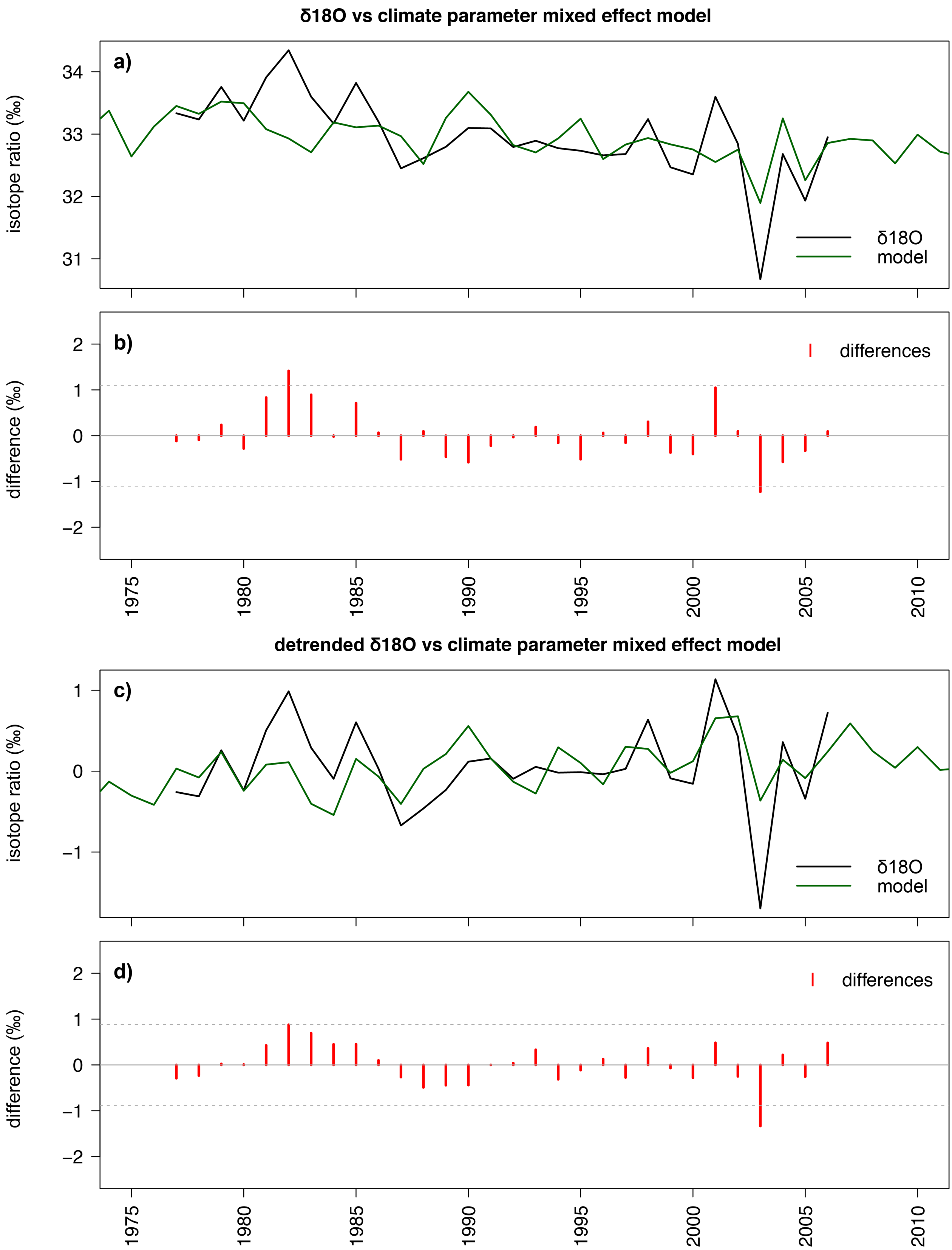

Figure 5-2 Raw and detrended $\delta^{18}O$ variability and the mixed effect models are shown in the top panels (a and c). The deviations between measurements and models (measurements - model) are shown in the bottom panels (b and d).

Radiocarbon - ^{14}C

Radiocarbon dating of our wood material is reported as fraction modern (F) following Reimer et al. (2004). Results are summarized in *Table 3*. Radiocarbon ages obtained from tree-ring material are in agreement with the atmospheric $F^{14}C$ along the calibration curve. The ^{14}C measurements of samples prepared by cellulose extraction indicate that for all years in the control period (1992 - 1996) as well as in the eruptive period (1999 - 2003) there was no evidence that trees had taken up fossil CO_2. The ^{14}C measurements of samples prepared with ABA also showed no depleted ^{14}C signal during the control period, but we found lower ^{14}C ratios in tree rings for 2001 and 2002, immediately before the eruptive period, suggesting that there could have been an uptake of fossil, ^{14}C-depleted, CO_2 by trees (*Figure 6*). We measured a second set of ABA-prepared samples to obtain additional measurement points and to verify that the reduced values before the eruption were not due to contamination. The two runs are consequently referred to as ABA1 and ABA2 (*Table 3*).

Dendro age	C14 age BP	±1σ	**F14C**	±1σ	δC13 ‰	±1σ	mg C	C/N	%C	**Preparation Method 1**	**Preparation Method 2**	**Site**
2003	-600	24	1.078	0.00	-24.8	1.1	0.98	59.26		soxhlet	cellulose	S1
2003	-624	24	1.081	0.00	-24.1	1.1	0.99	56.59		soxhlet	cellulose	S1
2003	-596	22	1.077	0.0029	-22.7	1	1	137.04		soxhlet	ABA 2	S1
2002	-607	24	1.078	0.00	-21.5	1.1	1.00	60.88		soxhlet	cellulose	S1
2002	-626	24	1.081	0.00	-23.0	1.1	1.00	53.22		soxhlet	cellulose	S1
2002	-353	24	1.045	0.00	-24.6	1.1	0.99	75.16		soxhlet	ABA 1	S1
2002	-342	24	1.043	0.00	-25.1	1.1	0.99	55.59		soxhlet	ABA 1	S1
2002	-641	22	1.0831	0.003	-23.6	1	0.99	125.81		soxhlet	ABA 2	S1
2001	-688	24	1.089	0.00	-23.4	1.1	0.99	53.32		soxhlet	cellulose	S1
2001	-675	24	1.088	0.00	-22.3	1.1	0.99	54.35		soxhlet	cellulose	S1
2001	-440	24	1.056	0.00	-21.9	1.1	0.99	63.98		soxhlet	ABA 1	S1
2001	-470	25	1.060	0.00	-25.6	1.1	1.00	65.02		soxhlet	ABA 1	S1
2001	-600	22	1.0775	0.003	-24.6	1	0.97	121.05		soxhlet	ABA 2	S1
2000	-749	24	1.098	0.00	-27.5	1.1	1.00	49.38		soxhlet	cellulose	S1

2000	-727	24	1.095	0.00	-22.8	1.1	0.99	54.07		soxhlet	cellulose	S1
2000	-730	22	1.0951	0.003	-24.3	1	0.94	114.64		soxhlet	ABA 2	S1
1999	-751	24	1.098	0.00	-21.1	1.1	0.98	59.96		soxhlet	cellulose	S1
1999										soxhlet	ABA 1	S1
1999	-749	25	1.098	0.00	-18.5	1.1	0.99	53.43		soxhlet	cellulose	S1
1999	-761	22	1.0993	0.003	-25.1	1	1	125.48		soxhlet	ABA 2	S1
1996	-897	24	1.118	0.00	-26.5	1.1	1.00	278.7	50.41	soxhlet	cellulose	S1
1996			0.000	0.00	0.0	1.1	0.00		0.00	soxhlet	cellulose	S1
1996	-884	24	1.116	0.00	-25.9	1.1	0.99	234.0	60.68	soxhlet	ABA 1	S1
1995	-933	24	1.123	0.00	-25.6	1.1	1.00	236.6	52.77	soxhlet	cellulose	S1
1995			0.000	0.00	0.0	1.1	0.00		0.00	soxhlet	cellulose	S1
1995	-909	24	1.120	0.00	-22.1	1.1	1.00	212.2	57.03	soxhlet	ABA 1	S1
1994	-967	24	1.128	0.00	-22.6	1.1	0.99	253.6	56.99	soxhlet	cellulose	S1
1994			0.000	0.00	0.0	1.1	0.00		0.00	soxhlet	cellulose	S1
1994	-915	24	1.121	0.00	-19.2	1.1	1.00	212.5	57.88	soxhlet	ABA 1	S1
1993	-997	24	1.132	0.00	-20.4	1.1	1.00	289.3	64.20	soxhlet	cellulose	S1
1993			0.000	0.00	0.0	1.1	0.00		0.00	soxhlet	cellulose	S1
1993	-1002	24	1.133	0.00	-20.2	1.1	0.99	193.6	59.05	soxhlet	ABA 1	S1
1992	-1034	24	1.137	0.00	-18.8	1.1	1.00	289.6	64.56	soxhlet	cellulose	S1
1992			0.000	0.00	0.0	1.1	0.00		0.00	soxhlet	cellulose	S1
1992	-997	24	1.132	0.00	-20.5	1.1	0.98	202.7	58.07	soxhlet	ABA 1	S1

Table 3 Radiocarbon measurements of single trees, expressed as the fraction of modern atmospheric ^{14}C (F14C).

The samples prepared by cellulose extraction do not deviate from the calibration curve and represent the atmospheric ^{14}C. Significant differences in $\Delta F^{14}C$ of three to four percent between cellulose-extraction prepared samples and ABA-prepared samples during the vegetation periods of 2001 and 2002 before the eruption are shown in *Figure 6*.

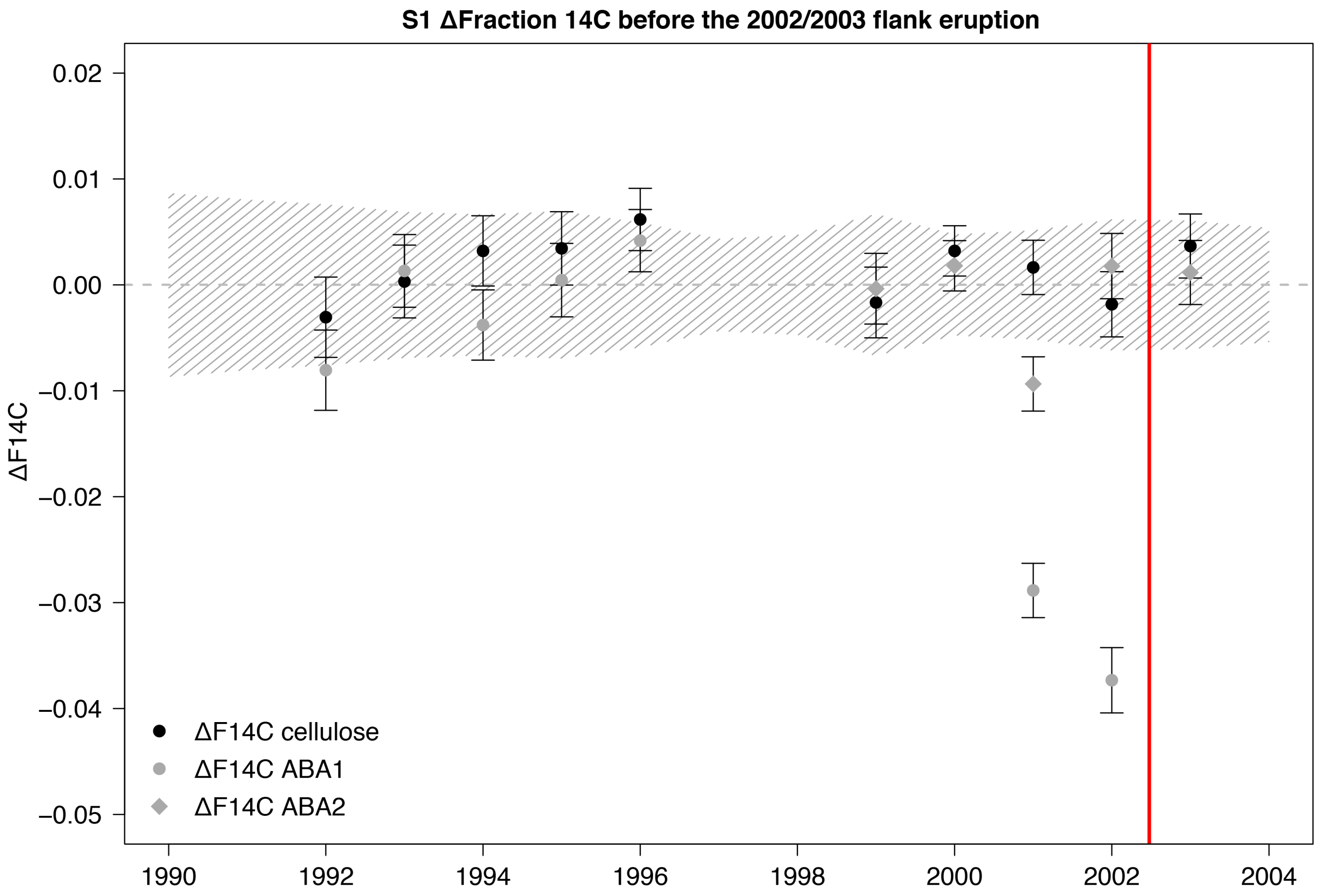

Figure 6 *Deviations of $\Delta F^{14}C$ values from both cellulose (black dots) and ABA (grey dots) preparation methods from the atmospheric composition (grey, interrupted line).*

Discussion

Stable isotopic ratios - $\delta^{13}C$ and $\delta^{18}O$

The generally positive relationship between carbon isotope ratios and temperature and the negative relationship with precipitation are in agreement with previously reported influences of climate on $\delta^{13}C$ (e.g., Porter et al., 2009), reflecting the positive influence of moisture on photosynthesis and stomatal opening (McCarroll & Loader, 2004). There were only minor differences between the raw and the detrended measurements, demonstrating that there was little influence of low-frequency variability on the isotope-climate correlations, and hence no substantial long-term trend in the data. During and after the eruption in 2002/2003, the $\delta^{13}C$ values were considerably lower than in the years before, suggesting an influence unrelated to climate variability and a possible influence by the ongoing volcanic activity on the carbon isotope ratio within the trees.

In contrast, the oxygen isotope correlations revealed a divergence in correlations between raw and detrended data. While there is a negative relationship between raw $\delta^{18}O$ and temperature (the opposite of commonly observed correlations; e.g., Reynolds-Henne et al., 2007), the detrended $\delta^{18}O$ data are positively correlated with temperature and negatively correlated with precipitation, in agreement with previous studies (e.g., Porter et al., 2009). The contrasting correlations with climate variables between raw and detrended stable oxygen isotope values clearly stems from low frequency variability, in which the long-term negative trend in $\delta^{18}O$ (*Figure 3*) is inversely correlated with an increasing temperature trend. On the other hand, after removing this long-term trend the detrended $\delta^{18}O$ data display the commonly observed correlations with temperature, which much more plausibly reflect the relationship between high-frequency variations in $\delta^{18}O$ and temperature, representing the direct influence of climate on $\delta^{18}O$ in the tree rings.

Positive $\delta^{18}O$ - temperature and negative $\delta^{18}O$ - precipitation correlations in the detrended $\delta^{18}O$ data are explainable by reduced stomatal conductance with higher temperatures, due to the strong isotopic enrichment of leaf water under such conditions (McCarroll & Loader, 2004). This commonly observed relationship also reflects the isotopic signature of the water source (usually precipitation), which depends on temperature due to fractionations in the hydrological cycle (Coplen et al., 2000) and the enrichment processes at the leaf level promoted by warmer temperatures and higher vapor pressure deficit (McCarroll & Loader, 2004).

Furthermore, the $\delta^{18}O$ values of 2003 are strongly negative compared to all other years preceding the event (*Figure 3*). Positive correlations between $\delta^{18}O$ and temperature suggest that either especially low temperatures in 2003 could have caused this reduced heavy oxygen signal, or that the water source used by the trees during that time was depleted in ^{18}O at our sample location on Mt. Etna. Temperature in

June, which shows the strongest correlation with $\delta^{18}O$, was above average in 2003, showing that the ratio was not reduced by low temperatures but must have been induced by the source water.

Indeed, it was reported that tree rings sampled about 40 km away from eruption sites contain lower oxygen isotope ratios after volcanic eruptions due to eruption-induced cloud coverage increasing relative humidity and reducing air temperatures (Battipaglia et al., 2007). This is however very unlikely in our case, because our samples were taken only 1 to 30 meters from the lava flows, implying that local ambient temperatures must have been increased rather than reduced during the event. More importantly, monthly average temperatures were not particularly low in 2003 and under similar temperatures between 1977 and 2002, no comparable reduction in oxygen isotopic ratios was measured. The same is true for precipitation variables. Therefore, the negative $\delta^{18}O$ values in 2003 among all trees (*Table 2*) are explained neither by climate variability nor by the climate model, suggesting that the significant reduction in the oxygen isotopic ratio may indeed have been induced by the ongoing volcanic eruption by deep water rising up to the surface.

Hereby, degassing of volcanic water vapor, which mixed with soil moisture, could have provided an additional water source causing a local increase in humidity close to the volcanic vent (Allen et al., 2002), thereby avoiding stomatal closure and altering isotopic ratios of the water source leading to a reduction in $\delta^{18}O$. This hypothesis is further supported by the reduced values in $\delta^{13}C$ during the same time (*Figure 3*).

In 2003, the trees may either i) have taken up an increased proportion of groundwater that was low in $\delta^{18}O$ compared to precipitation and surface waters (Giggenbach & Soto, 1992; Coplen et al., 2000; Kalbus et al, 2006; Balsch & Bryson, 2007), or ii) have incorporated ground moisture that condensed from volcanic vapor/gases (negative in $\delta^{18}O$; Ohwada et al., 2003) which provided an unusual water source. Hereby, the negative $\delta^{18}O$ of volcanic waters may be related to oxygen exchange between water and CO_2 gas (Caliro et al., 2005).

Significant changes in oxygen isotopic ratios induced by changes in tectonic settings before/during earthquakes on Iceland (Skelton et al., 2014) suggest that seismic activity before/during volcanic eruptions may similarly have altered groundwater composition on Mt. Etna by infiltration of volcanic water vapor into the shallow ground. Further, a recent study supporting this theory revealed that volcanic activity is likely to have led to an increase in soil moisture prior to a flank eruption on Mt. Etna (Seiler et al., 2017a). Therefore, we argue that heat radiation from the erupted lava together with additional water availability provided by degassing of volcanic water vapor (depleted in $\delta^{18}O$) may have led to moist conditions during the eruption of 2002/2003, which influenced stable isotope ratios in the 2003 tree rings. Under such conditions we would expect a higher stomatal conductance and subsequently reduced $\delta^{13}C$ ratios, consistent with the measurements reported here.

Radiocarbon - ^{14}C

Applying the cellulose-extraction preparation method, we did not find any evidence that trees had incorporated ^{14}C-depleted CO_2 during the eruption event of 2002/2003. However, applying the ABA preparation method, we found some deviations of $F^{14}C$ and negative $\Delta F^{14}C$ during two consecutive vegetation seasons (i.e., 2001 and 2002) before the 2002/2003 eruption. Since only three out of six ABA measurements prior to the eruption were reduced there is no clear enough evidence to conclude that trees did in fact take up ^{14}C-depleted CO_2 during two consecutive years preceding the surface eruption. However, the results insinuate that such an influence could be a possible explanation for the deviating values.

It has been reported that tree rings may contain lower $F^{14}C$ compared to the calibration curve in certain regions due to natural reservoir effects e.g., atmospheric circulation (Nakamura et al., 2013). While the different preparation methods (cellulose extraction and ABA) resulted in comparable radiocarbon ages between 1992 and 1999, we found disagreements for the years 2001 and 2002 only. Therefore, we argue that the deviation between cellulose and ABA prepared samples is unrelated to the preparation method. A previously reported deviation towards a younger ^{14}C age of samples treated with ABA compared to cellulose extraction was related to contamination by young ^{14}C induced by sample treatment (Southon & Magana, 2010). To prevent such contamination, we applied the soxhlet treatment, and it is unlikely that over two preparation runs the same years and no other years were contaminated twice. Interestingly, the reduced values were only observed among ABA prepared samples and not among samples prepared by cellulose extraction.

It is reported that re-filling of shallow conduits with magma can lead to pre-eruption CO_2 degassing and infiltration of CO_2 into soils (Aiuppa et al., 2013). Even though the results on ^{14}C are unclear, the studied trees may have been exposed to CO_2 degassing leading to reduced values of ^{14}C in the tree rings of 2001 and 2002 prior to the eruption of 2002/2003 because it corresponds to the time window during which the increased NDVI was observed (Houlié et al., 2006). Another explanation for the deviations could be that the annual pooling of wood material resulted in slightly unbalanced samples favoring material from one tree core. Nevertheless, would this imply that at least that one tree contained less ^{14}C than the others because the extracted material stems from the same growth season.

Conclusion

Given the obvious reduction in $\delta^{18}O$ in tree rings in immediate proximity to the eruption fissure, we conclude that it is likely that the 2002/2003 volcanic eruption impacted trees during and after the effusive eruption phase. A plausible explanation for the reduced $\delta^{18}O$ in the tree rings is the uptake of volcanic water during pre-eruption degassing.

Additionally, the reduced $F^{14}C$ values during two consecutive years exactly coinciding with the increased NDVI signal (Houlié et al., 2006) before the 2002/2003 eruption suggests that trees near the eruptive fissure may have taken up fossil CO_2 degassed during pre-eruption volcanic activity.

Our findings suggest that volcanic vapors (i.e., water vapor) reduced $\delta^{18}O$ values in tree rings after the eruption, and that warm and moist conditions caused by heat radiation of freshly erupted lava flows may have led to a reduction in $\delta^{13}C$ values in tree rings following the eruption. They further suggest that degassing of CO_2, in agreement with the reduced $\delta^{18}O$ values, may have reduced the ^{14}C content in tree rings of 2001 and 2002.

These results illustrate the potential impact of volcanic eruptions on stable isotope ratios in tree rings, and also establish photosynthetic response to pre-eruption CO_2 degassing as a possible explanation for local increases in NDVI before the 2002/2003 Mt. Etna flank eruption.

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